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Jas. Liddle
Glasgow University

INORGANIC CHEMISTRY

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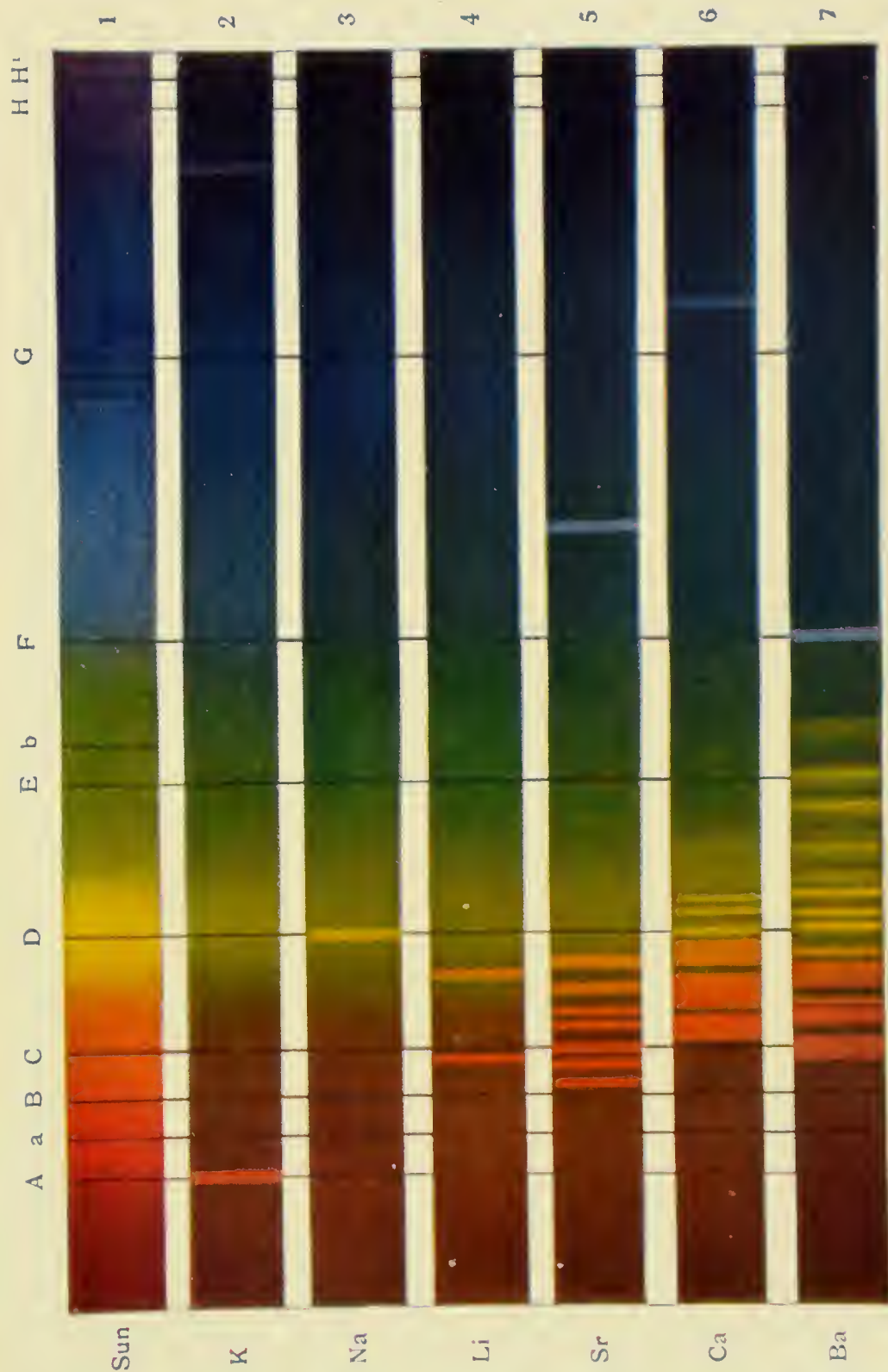


TABLE OF SPECTRA.

1, THE SOLAR SPECTRUM. 2, 3, 4, 5, 6, 7, THE SPECTRA OF POTASSIUM, SODIUM, LITHIUM, STRONTIUM, CALCIUM, BARIUM RESPECTIVELY.

THE ELEMENTS OF INORGANIC CHEMISTRY

For use in Schools and Colleges

BY

W. A. SHENSTONE, F.R.S.

LECTURER ON CHEMISTRY IN CLIFTON COLLEGE
AUTHOR OF 'THE METHODS OF GLASS-BLOWING,'
'A LIFE OF LIEBIG,' ETC.

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PREFACE TO THE FIFTH EDITION

THIS book was published four or five years ago with the hope that its earlier chapters might provide a course of experimental work for young beginners, and the later parts a textbook suited to the developed needs of the students as they grow older, and thus make it possible to avoid the inconvenience and waste of time involved, as science masters well know, in changing from an elementary book to an advanced book in the middle of the school course. Repeated calls, at brief intervals, for new editions and new impressions of the book encourage me to hope that I have in some degree attained this object.

Although only a little more than four years have elapsed since the first edition of the book was published, I have reason to believe that many of those who use it in their classes will welcome certain additions which are now made. In the year 1900 Qualitative Analysis, though assailed from many quarters, still reigned supreme in many, perhaps I might say in most, of the examinations at which the younger students of Chemistry compete. Hence it was necessary at that time to go slowly, to exercise considerable self-restraint in introducing the class of Laboratory work which I have advocated for the last quarter of a century. But impending changes in the competitions for admission to the

Army, the gradual improvement, if I may say so, of the practical exercises set in competitions for Scholarships at the Universities, and the probability that similar reforms will soon follow in other directions, have made it not only possible but necessary to introduce more practical exercises into the earlier sections of the book than seemed wise four years ago.

It is a great source of gratification to me that the changes alluded to in the previous paragraph are consistent in so considerable a degree with the original plan of my book, that they only make it necessary to slightly extend the scope of the practical work of Parts I and II and to add a little to the section dealing with the compounds of carbon, and that few alterations properly so-called seemed to be demanded.

In making the additions which, in my judgement, are required I have been careful to add and not to alter: and thus I feel sure these additions will not prove inconvenient in any way to those whose pupils already possess copies of the earlier issues. Everything that is in the earlier editions, with two or three exceptions, will be found in the present edition in the same sections, and on the same pages as before. Thus schemes of work founded on those earlier editions will apply equally well to the new one, except that the course of volumetric work has been extended, and I think improved, and Sections 295 and 296 enlarged and repaged. To secure this important object the book has not been repaged. The new matter has been introduced, with the two exceptions mentioned above, by adding a kind of appendix, at the end of Parts I and of II, by extending the

two above-mentioned sections dealing with Carbon, and by adding a new chapter at the end of the book.

In concluding these introductory remarks I may say that the chief additions now made are as follows :

First, a number of new practical exercises have been added to Parts I and II. These will be found at the ends of the respective parts. They deal with such subjects as the estimation of solids in solutions ; measurements of solubility ; quantitative and qualitative studies of the action of heat on substances ; determining the water in crystals ; preparation of salts and the method of crystallization ; the preparation of the common gases ; the determining of equivalent weights by gravimetric and volumetric methods ; gravimetric studies involving combination, decomposition and substitution, whilst the sections on Volumetric Analysis and Hardness have, I think, been improved and the scope of the former has been extended.

Secondly, the account of the Chemistry of the Carbon Compounds now includes sections dealing with oils, fats, soaps and the chief vegetable acids.

Thirdly, a chapter has been added at the end of the book on Radio-activity and Radium.

Finally, I have replaced the original Table of Atomic Weights by that issued a few months ago by the International Committee. I have given this table in its complete form, and teachers may find it desirable to warn their pupils that for many purposes the figures in the second place of decimals may be ignored. It seemed best on the whole to give the authoritative figures uncontracted. A few mistakes which

had previously escaped notice have been corrected, and the index has been extended.

In dealing with certain subjects, I have in this as in previous editions indicated by marginal lines some of the more difficult passages. The younger students will do well to omit these. A good deal of theory will be found in these marked passages; rather more perhaps than would be expected considering the main object with which the book was written. This theory is introduced with the hope that it may pave the way to the subsequent study of such books as Dr. Walker's *Elementary Physical Chemistry*, much as the latter, in their turn, are intended to lead on to the reading of more advanced treatises.

I should be ungracious if in launching this New Edition of my book I did not acknowledge my indebtedness to the kind suggestions I have had from several correspondents, and especially from my colleague, Mr. F. B. Stead, and to Mr. W. D. Rogers and Dr. F. D. Chattaway for several useful suggestions and much assistance at various times.

W. A. SHENSTONE.

CLIFTON COLLEGE,
Dec. 1906.

TABLE OF CONTENTS

METRIC WEIGHTS AND MEASURES	PAGE xii
---------------------------------------	-------------

PART I

CHAP. I. INTRODUCTION — COMBUSTION — INDESTRUCTIBILITY OF MATTER—CONSERVATION OF MASS	I
CHAP. II. INTRODUCTORY STUDY OF WATER	6
CHAP. III. PHYSICAL PROPERTIES OF WATER AND OTHER SUB- STANCES—MELTING-POINT—LATENT HEAT—BOILING-POINT —DENSITY	14
CHAP. IV. SOLUTIONS—LIQUID DIFFUSION—CRYSTALS	32
CHAP. V. COMPOUNDS — ELEMENTS — MIXTURES — CHEMICAL CHANGE	42
CHAP. VI. PHYSICAL AND CHEMICAL PROPERTIES OF WATER — SOLUTION—WATER AND THE METALS—OXIDATION AND RE- DUCTION—COMPOSITION OF WATER BY WEIGHT—HYDROGEN PEROXIDE—LAWS OF CONSTANTS AND MULTIPLES	53
CHAP. VII. ATMOSPHERE—BOYLE'S LAW—CHARLES' LAW—COM- PONENTS OF AIR—COMBUSTION—FLAMES—PLANTS, ANIMALS AND THE ATMOSPHERE—DECAY	70
FURTHER PRACTICAL EXERCISES ON SOLUBILITY OF SINGLE SUB- STANCES AND MIXTURES IN SOLVENTS AT VARIOUS TEMPERA- TURES—CRYSTALLIZING—FINDING WATER OF CRYSTALLIZA- TION—QUANTITATIVE EXPERIMENTS ON THE ACTION OF HEAT ON BODIES, THE PROPERTIES OF THE BODIES FORMED— PREPARING SALTS FROM ACIDS AND ALKALIS—PREPARING ELEMENTARY GASES	94

PART II

THE LAWS OF COMBINATION AND THE ATOMIC THEORY

	PAGE
CHAP. VIII. LAWS OF COMBINATION—CONSERVATION OF ENERGY —RECIPROCAL PROPORTIONS—GAY-LUSSAC'S LAW OF VOLUMES —EQUIVALENTS—ATOMS AND MOLECULES—MOLECULAR WEIGHTS—ATOMIC WEIGHTS—NOTATION—CALCULATIONS— VALENCY	95
CHAP. IX. CLASSIFICATION OF THE ELEMENTS—ACIDS, BASES, AND SALTS	127
CHAP. X. QUANTITATIVE STUDIES CONCERNING ACIDS, BASES, AND SALTS—VOLUMETRIC ANALYSIS	136
FURTHER PRACTICAL EXERCISES ON PREPARATION OF CHLORINE, HYDROCHLORIC ACID, AMMONIA, &c.—QUANTITATIVE EX- PERIMENTS, SYNTHETICAL AND ANALYTICAL—PREPARATION AND REDUCTION OF OXIDES—EQUIVALENT WEIGHTS—PRE- CIPITATIONS AND OTHER SIMPLE GRAVIMETRIC AND VOLU- METRIC EXERCISES	153 ^h

PART III

THE CHIEF NON-METALS AND THEIR PRINCIPAL COMPOUNDS

CHAP. XI. OXYGEN—OXIDES—OZONE	154
CHAP. XII. HYDROGEN—DIFFUSION OF GASES—LIQUEFACTION OF GASES—KINETIC THEORY OF GASES—OXIDATION AND REDUCTION	166
CHAP. XIII. INTRODUCTION TO THE 'PERIODIC LAW'.	179
CHAP. XIV. THE PROPERTIES AND PREPARATION OF THE HALO- GENS AND THEIR COMPOUNDS	184
CHAP. XV. THE PROPERTIES AND PREPARATION OF SULPHUR, SELENIUM, TELLURIUM, AND THEIR COMPOUNDS	225
CHAP. XVI. NITROGEN AND ITS COMPOUNDS—ARGON	256
CHAP. XVII. PHOSPHORUS AND ARSENIC AND THEIR COMPOUNDS	282
CHAP. XVIII. CARBON AND SILICON AND THEIR COMPOUNDS, INCLUDING OILS, FATS, SOAP, ALCOHOL, PARAFFIN, &c., &c.	308
CHAP. XIX. BORON AND ITS COMPOUNDS	358

PART IV

THE RELATION OF HEAT AND ELECTRICITY TO CHEMICAL
CHANGES. THE SPECTROSCOPE. CRYSTALLOGRAPHY

	PAGE
CHAP. XX. CHEMICAL AFFINITY—HEAT AND CHEMICAL ACTION	
—ELECTROLYSIS AND SOLUTIONS	360
CHAP. XXI. SPECTRUM ANALYSIS	379
CHAP. XXII. CRYSTALLOGRAPHY	383

PART V

THE METALS AND THEIR CHIEF COMPOUNDS

CHAP. XXIII. INTRODUCTION TO THE STUDY OF THE METALS .	388
CHAP. XXIV. LITHIUM—SODIUM—POTASSIUM—RUBIDIUM AND CESIUM—AMMONIUM	396
CHAP. XXV. CALCIUM—STRONTIUM—BARIUM	410
CHAP. XXVI. BERYLLIUM—MAGNESIUM—ZINC—CADMIUM . .	416
CHAP. XXVII. MERCURY	423
CHAP. XXVIII. ALUMINIUM—GALLIUM—INDIUM—THALLIUM .	427
CHAP. XXIX. TIN—LEAD—GERMANIUM	433
CHAP. XXX. ANTIMONY—BISMUTH	442
CHAP. XXXI. CHROMIUM	447
CHAP. XXXII. IRON—MANGANESE—COBALT—NICKEL . .	451
CHAP. XXXIII. COPPER	474
CHAP. XXXIV. SILVER	480
CHAP. XXXV. GOLD—PLATINUM	485
CHAP. XXXVI. RADIO-ACTIVITY AND RADIUM	490
APPENDIX I. THE BALANCE	496
APPENDIX II. CURVES OF SOLUBILITY	498
PROBLEMS	499
INDEX	505

METRIC WEIGHTS AND MEASURES.

PREFIXES.

Myria-	 10,000	()	 1
Kilo-	 1000	Deci-	 $\frac{1}{10}$
Hecto-	 100	Centi-	 $\frac{1}{100}$
Deka-	 10	Milli-	 $\frac{1}{1000}$

Inserting after the hyphen and in the brackets—

- (1) *Metre*, gives the measure of length.
- (2) *Litre*, „ „ capacity.
- (3) *Gram*, „ „ weight.

LENGTH.

- 1 **Metre** = 10 decimetres. (10 dcm.)
 = 100 centimetres. (100 cm.)
 = 1000 millimetres. (1000 mm.)
 1000 Metres = *Kilometre*.

CAPACITY.

- 1 **Litre** = 1 cubic decimetre. (1 c.dcm.)
 = 1000 cubic centimetres. (1000 c.c.)

WEIGHT.

- 1 **Gram** or the weight of 1 c.c. of pure water at 4° C.
 = 10 decigrams. (10 dg.)
 = 100 centigrams. (100 cg.)
 = 1000 milligrams. (1000 mg.)
 1000 Grams = 1 *Kilogram*.

ENGLISH EQUIVALENTS.

- | | NEARLY. | ACCURATELY. |
|--------------------|----------------------------------|------------------------------------|
| 1 Metre | = 3 feet 3 $\frac{3}{8}$ inches | = 39.37 inches. |
| 64 metres | = 70 yards (nearly). | |
| 25 mm. | = 1 inch (nearly). | |
| 1 Kilometre | = 1100 yards | = 1093.63 yards. |
| 8 kilometres | = 5 miles (roughly). | |
| 100 sq. metres | = 1 are | = rather less than 4 poles. |
| 1000 sq. metres | = 1 decaire | „ 1 rood. |
| 10,000 sq. metres | = 1 hectare | „ 2 $\frac{1}{2}$ acres. |
| 1 Litre | = 1 $\frac{3}{4}$ impl. pint | = 1.71 pint. |
| | or 35 ounces. | |
| 100 litres | = 22 gallons (nearly). | |
| 1 Gram | = 15 $\frac{1}{2}$ grains | = 15.43 grains. |
| 28 grams | = 1 ounce avoirdupois (roughly). | |
| 1 Kilogram | = 2 $\frac{1}{2}$ pounds | = 2.20 pounds. |
| Metric ton | = 1000 kilos. | = 19 $\frac{1}{2}$ cwt. (roughly). |

INORGANIC CHEMISTRY

PART I

CHAPTER I

INTRODUCTION

1. ALTHOUGH many of the chemical arts, such as glass-making, soap-making, and brewing, have been practised from very early times, the science of chemistry, in its present form, is of such comparatively recent origin that its foundations may be said to have been laid by Robert Boyle (b. 1626, d. 1691) in the seventeenth century. Experiments and observations were made in great numbers before the days of Boyle, but he perhaps more than any one else convinced chemists that real progress can only be made by combining experiments with the careful study of actual phenomena. Before Boyle taught, chemistry had been studied chiefly with the object of preparing medicines, or of improving the metals, and seldom solely for the sake of arriving at the truth. But Boyle, who looked at chemistry not merely as a physician and as an alchemist, sought to work out the fundamental principles of the subject. Thus he both indicated to chemists the true ideal of science, viz. to search after truth for truth's sake, and pointed out the only road by which this ideal can be approached.

2. The chemistry of fire. One of the subjects which especially interested Boyle and others was combustion. Their experiments on this subject showed that various things gain weight when they are burnt, and Boyle discovered, jointly with Hooke, that candles, sulphur, &c., will not burn in vessels which have been exhausted by an air-pump; but the meaning of these facts was not properly understood

until the French chemist Lavoisier (b. 1743, d. 1794) explained them by his theory of combustion.

3. Gain of weight and combustion. According to Boyle things gain weight when they are burnt. Let us test the truth of this statement in a few cases:—

EXPERIMENT 1. To learn if magnesium gains weight when burnt. Heat a gram of magnesium turnings in a small porcelain crucible, of known weight, by a Bunsen burner, raising the lid of the crucible frequently to admit air, but taking care that little or no white smoke escapes. When the metal is entirely converted into a white ash allow the whole to cool, and reweigh * the crucible and its contents.

EXPERIMENT 2. To find whether lead also gains weight when calcined. Repeat Experiment 1, using lead-foil. You must provide a short stirring-rod of iron wire for this experiment, and weigh it with the crucible. When the lead is melted, stir it frequently to expose fresh surfaces of metal.

If you perform the above experiments skilfully you will find that magnesium and lead do not lose anything when they are burnt, but, on the contrary, undergo an increase in weight. If you made a more extensive series of experiments you would find that this is not only true of other things which leave visible ashes, but that such substances as spirit of wine and oil also are changed into new and heavier substances when we burn them.

4. Lavoisier's researches on combustion. The results of the above experiments give rise to two questions:—What did the magnesium and lead absorb? and whence did they obtain it?

The answer to these questions was made clear by Lavoisier.

EXPERIMENT 3. To study the part played by air in the burning of charcoal. Heat a few fragments of charcoal, covered with sand, in two small crucibles to bright redness †. Empty the contents of one crucible whilst hot on to a plate, exposing the charcoal to the air, and observe what happens.

Continue to heat the other crucible for five or ten minutes, or longer, then expose its contents as before. In spite of the prolonged

* See Appendix, p. 490. As the work is intended to be done under guidance, descriptions of ordinary apparatus, such as crucibles, and of the methods of using it are omitted.

† A small muffle furnace should be provided for this and similar experiments.

heating you will find that the charcoal remains unburnt, until it is exposed at a red heat to the air.

The two facts that atmospheric air is required for combustion, and that things gain weight when they burn, suggest the idea that the air or some part of it may be absorbed in the process.

EXPERIMENT 4. To ascertain whether atmospheric air or any part of it is absorbed by a burning substance. Dry a globular flask *A* (Fig. 1) of about 200 cubic centimetres capacity, after draining it, by drawing a current of air through it, whilst warm, by means of a glass tube. Attach to *A*, by a cork *B*, a well-ground stop-cock *T**, or a piece of glass tube carrying a thick-walled india-rubber tube, closed by a small screw clamp. To assure yourself that the apparatus is air-tight, exhaust it with the mouth through *D*, and close *T*. After a few minutes re-open *T*. When you do this there should be a decided rush of air into the flask.

Place one or two small fragments of dry phosphorus† in *A*, close the flask with the cork, and weigh the apparatus, using as a counterpoise a flask similar to *A*, and adding either weights, small shot or grains of sand, to produce equilibrium. Cautiously warm *A*, near the part where the phosphorus lies, until the latter catches fire; when it ceases to burn allow the apparatus to cool and reweigh it. If the experiment has been done properly you will find the weight of *A* is unchanged. Now open the tap. When you do this you will probably hear air enter and will observe at once an increase in the weight of the flask and its contents. From these results it seems clear that phosphorus gains weight when it burns, and that it absorbs something from the air in the process.

After Lavoisier had satisfied himself, in 1774, that air is absorbed by sulphur and phosphorus when they burn, and by metals when they are calcined, he still remained uncertain what part of the air is absorbed in burning, and was unable to explain the reverse process by which calcined metals are reduced to the metallic state, until Joseph Priestley (b. 1733, d. 1804) and Scheele (b. 1742, d. 1786) independently



Fig. 1.

* Badly ground stop-cocks may be reground with emery powder moistened with turpentine in which a little camphor has been dissolved.

† The teacher must do this, and must heat the flask at the later stage, as accidents with burning phosphorus are apt to be followed by serious results.

obtained from red precipitate of mercury the colourless, odourless gas which possesses the power of supporting combustion in a truly remarkable degree, and which is now called oxygen. How Lavoisier turned this great discovery to advantage can be gathered from the following account of one of his experiments.

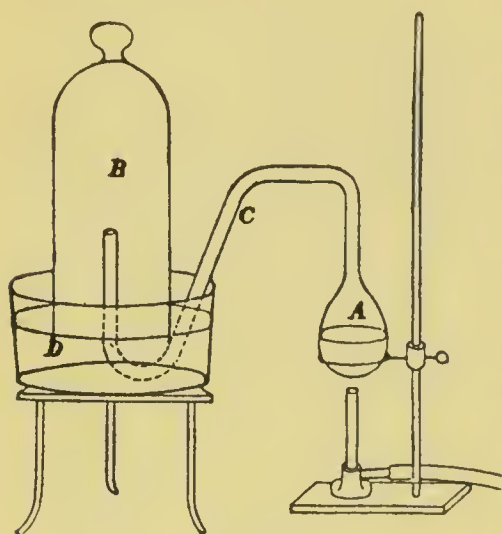


Fig. 2.

A was allowed to cool, and the air in *B* remeasured. It was found that $7\frac{1}{2}$ cubic inches had been absorbed. The red solid, which weighed

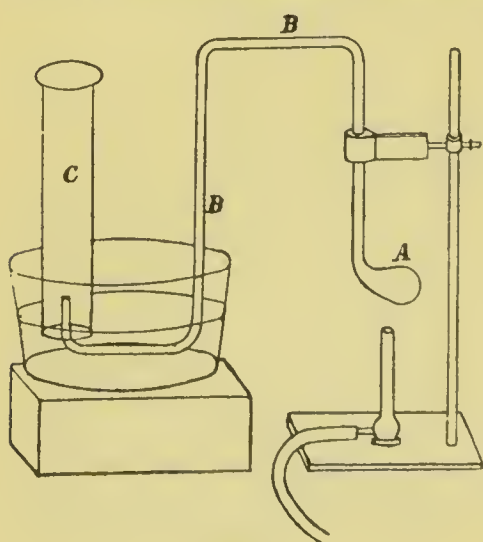


Fig. 3.

About 4 ounces of quicksilver were heated nearly to its boiling-point in a flask *A* (Fig. 2). *A* communicated by the tube *C* with a larger vessel *B*, which, together with *A*, contained 50 cubic inches of air, and stood in a basin of mercury *D*. Red solid particles gradually formed on the hot quicksilver. After several days, when this solid had ceased to form

45 grains, was collected, and heated in a glass tube *A* (Fig. 3). When thus treated the solid gradually disappeared and, simultaneously, mercury condensed on the cool parts of the apparatus. At the same time a gas escaped by *B*, and was collected in *C*, which had the qualities of oxygen. This gas measured about $7\frac{1}{2}$ cubic inches and the quicksilver weighed $41\frac{1}{2}$ grains. As $7\frac{1}{2}$ cubic inches of oxygen weigh, under the conditions of the experiment, $3\frac{1}{2}$ grains, it follows that the 45 grains of calcined quicksilver were

composed of $41\frac{1}{2}$ grains of quicksilver, together with $3\frac{1}{2}$ grains of oxygen, or *fire gas* as it was at first called. It was also evident that the oxygen came from the 50 cubic inches of air.

The gas left in *B* (Fig. 2) was unfit for respiration, and did not support combustion. But when it was mixed with the oxygen obtained from the red powder, it again became able to support animal life and combustion. Lavoisier thus satisfied himself that air contains two colourless gases, one of which is suitable for respiration, and able to support combustion, whilst the other is without these qualities. The latter gas is called *Nitrogen*. It had previously been recognized by Rutherford, and will be studied subsequently.

5. Is matter indestructible? Can we create it? It has been assumed, in the preceding pages, that a given increase in the amount of matter in a given vessel, let us say in a flask, can only be effected by actually transferring to the flask a corresponding amount of matter from some store previously existing elsewhere; and, conversely, that in order to effect a given reduction in the quantity of matter in any vessel we must transfer a corresponding amount to some new locality. And yet the first impression of any one who should watch a fire would be that the coal is utterly destroyed without any corresponding production of a new substance.

If we call to mind the result of Experiment 4, we shall remember that when phosphorus was burnt with a limited quantity of air in a well-secured flask, the weight of the flask, phosphorus and air taken, was exactly equal to that of the flask, burnt phosphorus and unused air at the end of the experiment; and that the increased weight of the burnt phosphorus was not detected until we admitted more air to replace that which had been absorbed. Does it not seem clear that, at the first stage of the experiment, the gain of the phosphorus was counter-balanced by a corresponding loss on the part of the air in which it was burnt? and that nothing was gained or lost by the acting substances, as a whole, during the changes which took place?

Again, let us consider Lavoisier's experiment (4). Lavoisier found that 50 cubic inches of air were diminished by $7\frac{1}{2}$ cubic inches after mercury had been heated in it. But these $7\frac{1}{2}$ cubic inches of gas were not destroyed; they were united with some mercury, forming oxide of mercury which gave back the same volume of gas when strongly heated.

Here again we see that the loss of the air corresponded in amount to the gain of the quicksilver, and that nothing was created nor destroyed in the experiment.

6. Principle of the conservation of mass. It would be impossible to examine every case of chemical change as described above. And even if we could do so, and used the most perfect instruments at our command for our experiments, it would still be impossible to be sure that no minute gains or losses had escaped detection. Nevertheless, chemists assume, as the basis of their work, that *the quantity of matter which takes part in each chemical change remains unaltered when that change is completed.*

No fact has yet been established which is inconsistent with the truth of this statement, and every accurate investigation made since the time of Lavoisier has confirmed this generalization, which, under the name of *the principle of the conservation of mass*, or *of the conservation of matter*, forms a part of the foundations of science.

The above brief account of the experiments and arguments by which Lavoisier laid the foundations on which chemists have built since his time is very imperfect. Its object, however, is not so much to give an exact account of the beginnings of chemistry, as to introduce some fundamental points to the student and, still more, to give him an idea of the manner in which discoveries may be made by means of experiments and the careful study of phenomena.

CHAPTER II

INTRODUCTORY STUDY OF WATER

7. Is water simple or compound? We have learnt that air contains at least two gases : oxygen, the supporter of life and combustion, and nitrogen which does not support life nor combustion. Let us endeavour to learn whether water is also a complex substance.

1. We know that when water is exposed to the air it quickly dries up, or evaporates. Let us see whether it evaporates completely, or whether a residue of some other substance is left.

EXPERIMENT 5. To learn if water leaves any residue when evaporated. Evaporate 10 c.c.* each of rain-water, spring water, and sea-water, or a mineral water, in three weighed dishes such as *A* (Fig. 4). The dishes should stand on iron wire gauze, and the Bunsen

* c.c. = cubic centimetre.

burner *B* should be turned low*. When the water has evaporated, examine the dishes closely, and reweigh them. You will find that spring water and sea-water differ from rain-water. The former leave more or less solid matter when they are evaporated, the latter little or none. Therefore, the former are not simple substances, though the latter may be.

2. We know that water can dissolve gases, for we have all seen the gas escape from a bottle of soda-water on opening it. Therefore, it seems possible that rain-water which has been much exposed to the atmosphere may contain air, although it contains no solid matter.

EXPERIMENT 6. To learn if rain-water contains dissolved air. Fill

a flask *A* (Fig. 5), capable of holding about 500 c.c., to the brim with rain-water. Attach a delivery tube *B* to *A*, taking care that *C* is partly filled with water. Boil the water at *C* to expel all air from *B*. Then heat the contents of *A*, after placing the receiver *D*, filled with water, over the end of *B*.

If the experiment be properly made, air will collect in *D*, and if the experiment be repeated with other natural waters, similar results will be obtained. Therefore, it is clear that ordinary water is not a pure substance; the greater part of it consists of a volatile liquid, but it also contains either solid matter and gas, or one of these, in small quantities.

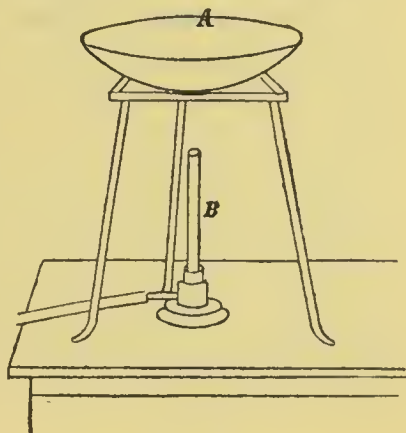


Fig. 4.

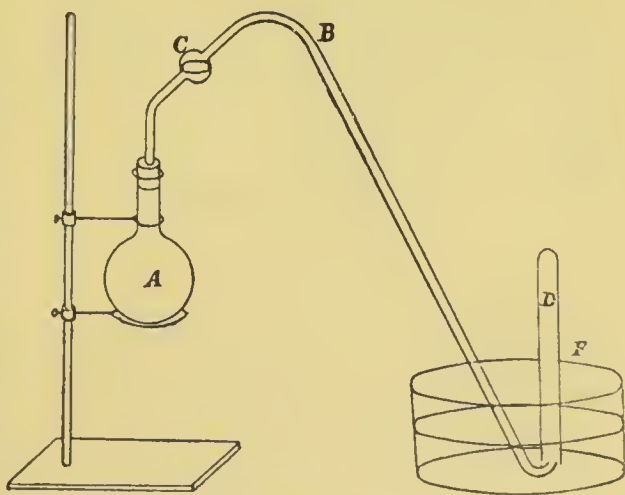


Fig. 5.

* When several similar experiments must be made, as in this case, it is convenient to divide them among the class, in order to economize time and apparatus.

We have still to learn whether the volatile liquid is a single substance, but we may postpone the consideration of this question for a little while.

8. Pure water. How to obtain it. Distillation. You will now understand that when chemists need pure water they must prepare it by a special process, since even rain-water is not quite pure, though it contains but little solid matter.

Water is easily converted into steam by heat; it leaves behind dissolved solids when it evaporates, and, as we have seen, it readily gives off any gas it may hold in solution when it is heated. Therefore, if we want water free from solids and gases, we must boil a natural water and recondense the steam. Further, we shall do well to reject

the first portions condensed, as the dissolved gases are given off with them, and we ought not to evaporate all the water, because towards the end of the process some of the residue, in which the solids are concentrated, may be projected mechanically into the steam, and so contaminate the product.

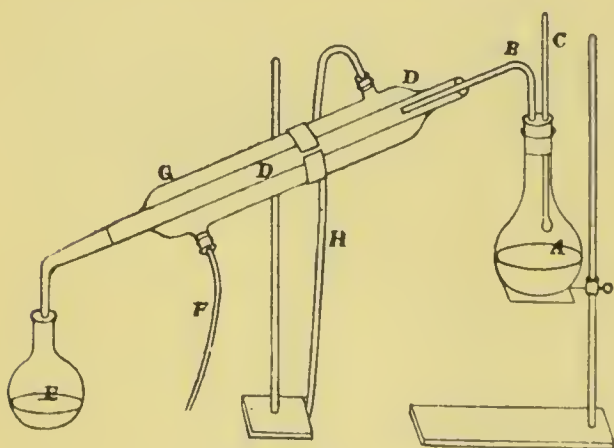


Fig. 6.

EXPERIMENT 7. To purify water by distilling it. Place some spring or rain-water

in a flask *A* (Fig. 6) fitted with a cork carrying a tube *B*, and a thermometer *C*. Connect *B* with the inner tube *D* of a 'Liebig's condenser' as in the figure, and let the lower end of *D* pass to a receiver *E*; supply cold water to the outer tube *G* of the condenser from a tap by *F*, and let the overflow pass by *H* to a sink. Heat the water in *A*. When it boils, observe *C* at intervals; you will find that the temperature remains *steadily* at about 100° . Reject the first part of the distillate. (Why?) Then collect two-thirds of the remainder. (Why no more?) Evaporate in basins a few drops of the respective contents of *A* and *E*. You will find that the distilled water leaves far less solid matter than that which remains in *A*.

Chemists usually employ distilled water for their experiments. If the water is wanted in a highly purified state it is condensed in a platinum tube, for platinum is not attacked by water, and preserved in vessels of platinum or silver. Air may be got rid of, as we have seen, by boiling the water. Distilled water is usually made by condensing steam, generated in copper boilers, in tubes of tin which are kept cool by cold water. You can probably see such a 'still' in action in the laboratory.

9. Natural waters. Owing to the solvent powers of water it is impossible to obtain a pure natural water; even rain-water contains traces of solid matter derived from dust, as well as gases, whilst the water of springs, and rivers, which has been in contact with earth, contains solid matter in much greater proportions. It is not difficult to understand why there is more solid matter in sea-water than in spring water. Rain, after passing over or through the earth, finds its way to springs, brooks, and rivers, and thus passes to the sea carrying with it matter extracted from the rocks with which it has come into contact. This water does not, however, stay permanently in the sea, for constant evaporation goes on, especially at the hotter parts of the world, and thus the solid matter is left in the sea as it was left in the dish, Experiment 5. But further, the evaporated water does not remain permanently in the air; sooner or later it is redeposited on the land as rain, hail, or snow, and so again passes to the sea recharged with solid matter. Thus the ocean must constantly gain solid matter at the cost of the land.

The following table shows how the proportions of solid matter in natural waters vary:—

Total weight of Solids in 100 litres of various Natural Waters.

Rain-water . . .	3.5	grams.	Black Sea . . .	1,750	grams.
River Neva . . .	5.5	„	Indian Ocean . .	3,400	„
„ Rhine . . .	16-30	„	North Atlantic .	3,850	„
„ Thames . . .	30-40	„	Dead Sea . . .	24,000	„
„ Jordan . . .	105	„			

Questions. 1. How do you account for the amounts of solid matter in the waters of the Rhine and the Thames respectively differing so widely?

2. Look at a map and endeavour to find a reason for the freshness of the waters of the Black Sea, and the exceptional saltiness of those of the Dead Sea.

The following table, which should *not* be learnt by heart, will give some idea of the nature of the solids which occur in sea-water.

Amount of each substance in 1,000 parts of Sea-water from the Irish Channel. (Thorpe and Morton.)

Common salt (sodium chloride)	26.44	Calcium sulphate	1.33
Potassium chloride . . .	0.75	„ carbonate	0.05
Magnesium chloride . . .	3.15	Lithium chloride	trace
„ bromide	0.07	Ammonium chloride . . .	trace
„ sulphate	2.07	Iron carbonate	trace
„ carbonate	trace	Silica (the component of sand)	trace
„ nitrate	trace	Total	<u>33.86</u>

10. Spring water and river water. The nature of the solids in the water of a spring must depend on the character of the soil and rocks with which that water has come into contact on its way to the spring. If, for example, the water has passed over rocks containing comparatively little soluble matter, we shall obtain a comparatively pure water from the spring. If, on the other hand, it has passed through beds of chalk it may be rich in lime (279). A water which is so charged with saline matter or gases as to be unfit for domestic use is called a *mineral water*. Some mineral waters are very valuable. A good many, as for example those of Bath and Harrogate, are useful medicinally, whilst others supply us with rare and useful substances.

River water like spring water also contains dissolved solids, but as much of the water of a river may be surface water, that is, may have come into the river without penetrating far into the earth, river water often contains a smaller proportion of solid matter than that of springs. This is especially the case when the river flows through a country where the rocks are hard and insoluble, like granite.

Although the proportion of solid matter in river water may seem small, yet the total amount carried away by a large river is very great. Thus, according to Professor Prestwich, the Thames at Kingston discharges daily 1,250,000,000 gallons of water. Every gallon of this water may be taken to contain 19 grains of solid matter in solution. $1,250,000,000 \times 19$ grains amounts to about 1,502 tons, which shows us that about a ton of solid matter per minute, or 548,230 tons per annum, are carried to the ocean by this one river.

Although river water is more free from saline matter than spring

water, it is not always more wholesome, because, apart from the sewage that we wastefully throw into our rivers, a river water is apt to contain organic impurities derived from the decomposing vegetable and animal matter on the surface of the land drained by the river; and though the water of a running stream gradually effects its own purification and becomes fit to drink, yet before this process of purification is complete it is by no means certain to be wholesome.

11. Hardness of water (see also p. 318). Digest some thin shavings of soap with distilled water in a warm place for some hours, shaking occasionally, and decant the clear liquid from the sediment *. Then add some of the soap solution little by little from a measuring-glass, shaking well, to some distilled water, and also to some solution of calcium sulphate †. Observe which requires most soap to make it give a permanent froth, i.e. a froth which remains for five minutes when the water is still.

A water which refuses to give a froth until much soap has been added is called **Hard Water**.

That which froths with very little soap is said to be **Soft**.

The behaviour of hard water with soap may be explained as follows. Soap may be regarded as a kind of salt. It is made by boiling oil with caustic soda. Hard water contains compounds of calcium or magnesium which act upon soap, producing insoluble substances. Thus the soap is destroyed, it does not remain in the water at all and so cannot give a frothing solution. The insoluble substances are formed continuously until all the magnesium and calcium in the water have been precipitated. After this point is reached any further soap that may be added remains in the solution, and the water will give a froth if it be well shaken.

The presence of these compounds of calcium and magnesium in water leads, as may easily be imagined, to the waste of great quantities of soap, and it is therefore important to be able to soften hard waters.

Questions. 1. Consider what you have learnt about water and suggest *two* methods for softening hard water.

2. Describe exactly how you would compare the hardness of the waters from

* Seven grams of good curd soap dissolved in a litre of water will give a suitable solution. If you wish to preserve the solution for future use, substitute proof spirit for the water.

† This may be prepared by shaking plaster of Paris with water, and filtering the solution.

two different rivers. Then compare the hardness of the two samples of water given you for the purpose and state the results you obtain.

Temporary Hardness. Permanent Hardness. Obtain some ordinary tap-water if it is suitable, or, if not, get some water prepared for the experiment from the Laboratory Attendant. Measure out 50 c.c. of it and boil it in a flask. Meanwhile, measure out another 50 c.c. of the water, and add soap solution in portions of 1 c.c. at a time from a measuring-glass or burette, shaking well after each addition, until it gives a permanent froth, and note the volume of soap required for this purpose.

After the first portion of the water has boiled freely for ten minutes *, dilute what remains with distilled water to 50 c.c., and add soap, shaking as before. Now state:—

- (a) How much soap was required by 50 c.c. of unboiled water.
- (b) How much soap was required by 50 c.c. of boiled water.
- (c) What proportion of the hardness was destroyed by boiling.
- (d) What proportion of the hardness was left after boiling.

The hardness which remains after boiling is called *permanent hardness*.

The hardness destroyed by boiling is called *temporary hardness*.

The former can be produced artificially by dissolving any soluble compound of the metals calcium or magnesium in water. Verify this, using very little of the salt selected, say calcium chloride or sulphate.

To produce temporary hardness in water pass a rapid stream of carbon dioxide (279, 2) through some water in a flask, after adding a little chalk, for five minutes, then filter the water. Examine the behaviour of 50 c.c. of the product with soap solution.

Boil another portion for some time, testing the steam as it escapes for carbon dioxide (280, 4 and 5), and finally test the boiled water with soap. You will find:— (i) That carbon dioxide escapes from the water during ebullition, and that a solid deposit forms. This deposit consists of calcium carbonate (384), and if enough can be collected on a filter it will be found to give off carbon dioxide like chalk does when an acid is added to it. (ii) That after prolonged boiling the water becomes soft.

The solid crust, or fur, which forms in kettles and inside the boilers of steam-engines, consists, for the most part, of the carbonates of

* It should really be boiled much longer, say for an hour. But you may be unable to find time for this.

calcium or magnesium which have been deposited from boiling water, like the sediment in the last experiment.

Questions. 1. Would not a certain amount of soap be required to make pure distilled water give a permanent froth? Try whether this is the case. Having done so, reconsider the results of the previous experiments, and state more exactly:—

(a) The total hardness of the water.

(b) The temporary hardness.

(c) The permanent hardness.

2. Compare your results with those of the other workers to ascertain whether they all agree exactly, or whether some results are too high, and others too low:—

How can you correct for these ‘*errors of experiment*’?

3. Make the correction in the manner proposed, and state the final results of your experiments.

Corrosion of limestone rocks. The power of dissolving carbonates of calcium and magnesium possessed by water containing carbon dioxide, enables it to dissolve solid rocks composed of these substances. When the solution so formed is exposed to the air, the carbon dioxide slowly escapes and the carbonate of calcium is deposited once more. Such deposits often occur in limestone caves, which then present a very beautiful appearance, their roofs, walls and floors being covered with *stalactites* and *stalagmites* in varied and fantastic forms. *Stalactites* are the masses which hang from the roofs of the caves; whilst the *stalagmites* rise from the floor to meet them. Destructible objects are sometimes fossilized and preserved by the action of water containing carbonates.

Softening hard water. If the hardness of a water is temporary, Clark’s method of softening it is usually restored to. This consists in adding as much lime to the water as will combine with the carbon dioxide present. Calcium carbonate is formed and precipitated together with the carbonates previously held in solution (280). If you add lime-water to some of the hard water prepared from lime-water as above described, you will at once get such a precipitate, and if you add the right proportion of lime you will soften the water completely.

Permanently hard water can also be rendered soft by chemical means. In the laundry sodium carbonate* is used. This throws the calcium and magnesium out of solution in the form of carbonate.

A further account of the action of hard water on soap and of the nature of soap will be found on page 338.

* Soda crystals, 357.

CHAPTER III

SOME PHYSICAL PROPERTIES OF WATER AND OF OTHER SUBSTANCES

12. Physical and chemical changes. The following experiments must be made by the student, in order that he may learn to distinguish the *physical properties* of substances from their *chemical properties*.

EXPERIMENT 8. To compare the effect of heating platinum and magnesium in air. 1. Weigh a piece of platinum wire or foil, heat it strongly for some time in a crucible, allow it to cool, reweigh it, and examine its appearance.

2. Make a similar experiment, using a piece of magnesium wire or, better, repeat Experiment 1.

On comparing your results you will find they differ. Though the platinum was heated as strongly as the magnesium it returned to its original state on cooling, and its weight remained unaltered at the end of the experiment. The magnesium, on the other hand, gained considerably in weight and no longer looked like magnesium, nor indeed like a metal at all, but was changed into a white non-metallic earthy solid.

We have here a simple illustration of the difference between physical and chemical changes. In the first case, there was no change of weight, the platinum gained nothing and lost nothing; it became hot and luminous for a time, but it was not permanently changed in regard to any of its properties. This was an example of physical change.

In the second case the magnesium united with oxygen from the air to form a new substance quite unlike either of those from which it was formed, which weighed more than the magnesium taken to produce it. This change was a chemical change.

Exercises. 1. Place a little dry oxide of mercury in a test tube; plug its mouth loosely with glass-wool to prevent the escape of solid particles; weigh the tube and its contents. Heat the oxide of mercury for some time pretty strongly, observing what happens, then cool, reweigh and describe your observations. Is the change a chemical or a physical change?

2. Make a similar experiment with a little red iodide of mercury. After cooling and reweighing allow the residue to remain in the test tube at least a day before you make your final observations. Explain if the changes which occur are chemical or physical changes.

3. Rub a few particles of iodine with a very small globule of mercury and a drop or two of alcohol in a mortar. Observe what happens. Is the change a chemical or a physical one? Give reasons for your answer.

From the foregoing you will gather that when two substances, such as air and magnesium, or iodine and mercury, interact to produce one or more new substances, or when a single substance such as oxide of mercury divides into two or more new things, we call the change a chemical change. Thus ordinary cases of combustion, in which the thing burnt unites with oxygen from the air, are chemical changes.

Familiar examples of physical change are the converting of bars of iron or steel into magnets, of water into ice or steam and, vice versa, the change of ice or steam into water. (See also 47.)

13. The melting-point of ice. We all know that ice is melted by heat, and that after a thaw it is only formed again if the temperature falls below 0° .

EXPERIMENT 9. **To find the melting-point of ice.** Place some crushed ice in a jam-pot or beaker, plunge the bulb of a thermometer in the ice, warm the whole very gently over a very small flame, stir constantly, and read the thermometer at short intervals. When all the ice has melted, but not before, compare your observations with what follows. You should have noticed that, though heat was continuously supplied to the ice and water, its temperature did not begin to rise above 0° until most of the ice was melted. 0° is accordingly called the *melting-point* of ice.

14. Amount of heat required to melt one gram of ice. We have just seen that heat disappears when a solid is melted; and it may be mentioned that it has been ascertained that if a gram of ice is converted into water at 0° , as much heat is absorbed as would suffice to raise the temperature of 79 grams of water from 0° to 1° . This quantity of heat is called the *latent heat of liquefaction of ice*.

Other solids when melted also absorb heat, and the heat absorbed is called *latent* (or *hidden*) *heat of liquefaction* or *of fusion*. This heat is evolved again when the liquid is resolidified. The following experiment illustrates this latter point.

EXPERIMENT 10. **To observe the evolution of heat which occurs when a liquid solidifies.** Place some crystals of thiosulphate of soda in a clean flask, plug the mouth of the flask with cotton-wool, and immerse it in water heated to 60° ; when the salt has melted, place the flask on a pad of blotting-paper, and allow it to cool without shaking; then

remove the cotton-wool and introduce a thermometer bearing upon it a minute fragment of the thiosulphate. When you do this the liquid will quickly crystallize, and the thermometer will rise rapidly, owing to the evolution of heat that accompanies the solidifying of the salt.

15. The boiling-point of water. EXPERIMENT 11. To ascertain the temperature at which water boils (see also Experiment 17). Place a thermometer in a flask partly filled with water and standing on a tripod stand over a Bunsen burner. It is a good plan to put a short piece of india-rubber tube over the tip of the bulb of the thermometer as it is then less likely to break, or be broken by, the bottom of the flask. Heat the water till it boils freely and read the thermometer frequently. Then compare your observations with what follows. The thermometer rises until the water begins to boil; it then stands at about 100° , but rises no higher. If you increase the supply of heat the water boils more quickly *, but the thermometer does not rise; for just as heat is absorbed, or rendered latent, when ice is melted, so some heat is rendered latent when water is evaporated; and just as this absorption of heat prevents us from heating a mixture of ice and water above 0° , so does the absorption of heat which accompanies the boiling of water prevent us from heating it above its *boiling-point* †.

16. Latent heat of vaporization of water. The heat thus rendered latent is called the *latent heat of vaporization of water*, or generally, for other liquids exhibit similar phenomena, *latent heat of vaporization*. It was stated above (14) that when one gram of ice at 0° is converted into water at 0° , as much heat is absorbed as would be required to raise 79 grams of water from 0° to 1° . Similarly if we evaporate a gram of water, a definite amount of heat will be required for the work. Moreover, the heat thus rendered latent can be recovered, as in the previous case, if the steam is recondensed.

EXPERIMENT 12. To observe the evolution of heat which occurs on condensing steam, and to measure its amount approximately. Half fill a half-litre flask A with water, add some frag-

* If the water refuses to boil quietly, but remains quiescent and enters into almost explosive ebullition alternately, add a few fragments of broken pipe stem. These will carry some air in their pores and promote steady boiling for a time.

† The exact temperature at which water boils varies. Pure water boils at 100° when the barometer stands at 760 mm.

ments of pipe stem, and attach a delivery tube *B* provided with a trap *C*. Heat the water in *A* till it boils. When all the air is expelled from the flask, allow the steam to pass into 100 grams * of water cooled to 0°, and placed in a thin glass flask capable of holding 200 c.c., supported inside a beaker on three small corks. At first the steam will condense, raising the temperature of the water, but after a time the temperature of the latter will reach 100°, and then the steam will escape freely. As soon as this occurs, close the mouth of the flask loosely, allow it to cool and then reweigh or measure its contents. You will find that it contains about 120 grams of water; therefore 20 grams of steam at 100° in condensing to 20 grams of water at 100° give out sufficient heat to raise 100 grams of water from 0° to 100°.

Now the heat required to raise 1 gram of water 1 degree (strictly from 0° to 1°) is called a 'unit of heat' †; therefore the heat required to raise 100 grams of water to 100° amounts to 100×100 units. It follows that 20 grams of steam at 100° in condensing to water at 100° give out 10,000 units of heat; therefore 1 gram of steam at 100° in condensing to water at 100° must give out $\frac{10000}{20} = 500$ units of heat.

But if it be admitted that no heat was created or destroyed in our experiment, these 500 units of heat must have been absorbed in the production of 1 gram of steam at 100° from 1 gram of water at 100°. We thus find the *latent heat of evaporation* of water to be 500. The true number is 537, the difference being due partly to the fact that we have ignored the heat required to warm the flask, partly to loss of heat by radiation, and partly to what may be called 'errors of experiment.'

17. Errors of experiment. If several students make the above experiment independently, or if a single student repeat it several times, the results obtained will differ from one another in a greater or less degree, owing to what are called 'errors of experiment.' The

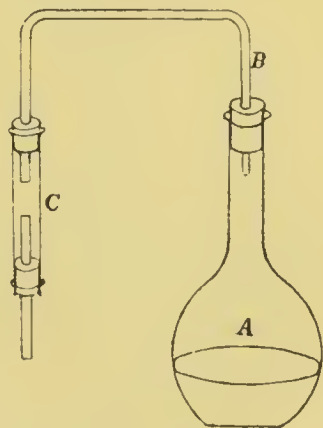


Fig. 7.

* Approximately 100 c.c.

† Or a calorie.

magnitude of these errors may be reduced by practice, and by the use of superior instruments, but they cannot be got rid of altogether.

When a number of similar experiments are made, it is likely that some of the results obtained will be 'high,' that is above the true value, and others 'low.' Therefore it is best not to trust the result of any single experiment, but to take the 'mean' of several. For example, let us suppose that *A*, *B*, *C*, and *D*, separately perform Experiment 12, and obtain the values which follow—

I.	II.
Experimenter.	Heat of vaporization found.
<i>A</i> .	520.
<i>B</i> .	530.
<i>C</i> .	550.
<i>D</i> .	540.

Then by dividing the sum of these four numbers by four they find 535 to be the heat of vaporization of water.

When a group of students have occasion to make the same experiment at the same time, it is a good plan to combine the results obtained in this way.

18. Recognizing substances by their physical properties.

We have seen that ice cannot be heated above 0° under ordinary conditions, nor water much above 100°, and the question naturally occurs to us—Might we use these qualities of water as a means of identifying the substance? and, again, Do other substances also melt and boil at fixed temperatures, which might be used as a means of identification?

It would be impracticable for a beginner to learn the answer to these questions by actual experiments. Therefore it must suffice to say that water, and many other substances, can be distinguished from one another by their melting-points, boiling-points and other physical properties. As it is not always convenient to use large quantities of material, special methods such as the following are usually employed.

19. Finding the melting-points of solids. EXPERIMENT

13. To find the melting-point of phosphorus (Fig. 8). Get your instructor to place a small fragment of phosphorus in a narrow tube *A*, cover the phosphorus with water, tie *A* to a thermometer *T*, as in the figure, plunge them into a beaker *B* containing cold

water, and warm the water very gradually. As soon as the phosphorus begins to melt notice the temperature of the water.

As you may overshoot the mark at the first attempt, you may treat the first experiment as a preliminary one, working rather quickly, and then make a fresh observation with greater care. For the final experiment use a fresh specimen of phosphorus, and stir the water in *B* diligently to keep its temperature uniform. If your work is accurate you will find that phosphorus melts at about 44° .

If a considerable quantity of the solid is available, its melting-point or freezing-point may be found by immersing the bulb of a thermometer in some of the melted solid in a test tube, allowing them to cool, reading the thermometer at intervals and stirring the liquid frequently. The thermometer will fall till solidification begins, then remain steady until the solidification is complete, and finally will slowly fall to the temperature of the air. The point at which the temperature remains constant is the melting-point or freezing-point. If the observations are made at short intervals and marked on squared paper they give an instructive curve (30). The substance may fall below its melting-point before it solidifies (superfusion), in which case the temperature will rise to the melting-point as soon as solidification sets in.

The student should now find the melting-points of a few other substances such as crystallized carbolic acid, sulphur, sodium, stearic acid, picric acid, urea.

When the substance whose melting-point is required melts at a higher temperature than 100° some other liquid than water must be used in *B*. A bath of quicksilver, melted paraffin, or melted sulphur, or one of molten lead or zinc may be used. The following table will give some idea of the range of the approximate melting-points of various solids :

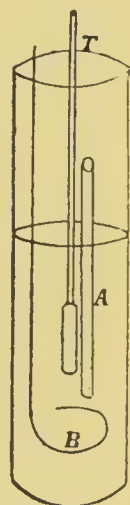


Fig. 8.

Table of Melting-points.

	C.		C.
Mercury	-39°	Lead	330°
Ice	0°	Zinc	420°
Phosphorus . . .	44°	Table salt . . .	770°
Sulphur	115°	Silver	about 950°
Tin	230°	Gold	„ 1050°

20. Melting-point a test of purity. The melting-point of a substance not only helps us to identify it, but also affords us a means of testing its purity, owing to the fact that mixtures tend to melt at lower temperatures than their components. Hence if a given substance fuses below its reputed melting-point it is likely to be impure.

The same fact helps us to understand why sea-water and brine are more difficult to freeze than pure water. Sea-water is a mixture of salt and water; water melts at 0° , and salt at about 770° , but a mixture of the two melts below 0° and therefore only freezes when it is cooled below this temperature.

EXPERIMENT 14. Compare the melting-points of lead, tin, bismuth, and cadmium with that of 'fusible metal,' which is a mixture of these four metals. Place fragments of the five substances in five small tubes, place these tubes in cold water as in Experiment 13, warm the water and notice that only the mixture melts below 100° .

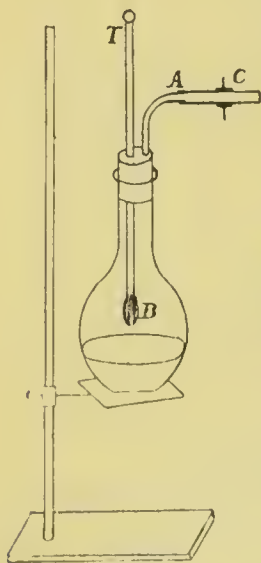


Fig. 9.

21. Atmospheric pressure and boiling-point. **EXPERIMENT 15.** To find the boiling-point of a liquid. Fit a cork carrying a thermometer T and a tube A to a flask B , containing water, as in Fig. 9. Heat the water till it boils. When steam escapes freely from C , read the thermometer.

If the thermometer be correctly graduated, and if the barometer stand at 760 mm., the temperature of the steam will be 100° . But if the barometer stand much above or below 760 mm., then the temperature of the steam will be a little higher or lower than 100° .

What is the meaning of this? How is the height of the barometer connected with the boiling-point of water?

As the mercury in the barometer cannot be supposed to exercise any control over the boiling of water in a distant flask, there must be some common cause connecting the two phenomena. You have no doubt heard that we live at the bottom of an ocean of air which extends far above us. May not this sea of air control alike the boiling of liquids and the position of the mercury in our barometers, since both are immersed in it? Let us make an experiment, in imitation of one

made by Boyle, in order to learn if changes in the pressure of the air influence the height of the barometer.

EXPERIMENT 16. To find whether the mercury in the barometer is supported by the air. Obtain a piece of stout glass tube about 10 mm. in diameter, and bent as shown in Fig. 10, so that its closed arm *AB* is about a metre in length. Introduce dry mercury at *D*, and manipulate the tube so that the quicksilver passes into *AB*. When *AB* is nearly full invert the tube and remove air bubbles as completely as possible by tapping and shaking it; then fill it up with mercury to *E*, removing all air bubbles from the bend, and place the tube in the position shown in Fig. 10. The mercury will at once fall in *AB* and rise in *AD*, forming a kind of rough barometer.

Now if, as was supposed by Boyle, the column of mercury in *AB* is supported by the pressure of the air on the exposed surface of mercury in *AD*, then sucking air from *AD* should cause the mercury to fall in *AB*. Attach an india-rubber tube at *D* and remove the air, as far as you can, by sucking with the mouth or, better, by means of an air-pump. As you do this the mercury will fall in *AB*, and if you remove all the air from *AD* it will stand at the same level in both arms. If you then admit air to *AD* again the mercury will once more rise in *AB*. Finally, if you blow air into *AD*, you will force the mercury above its original level in *AB*.

These various results lead us to conclude that the mercury in our barometer is supported by the pressure of the air, and that changes in the height of the mercury must indicate alterations in the pressure of the air.

Now let us see if variations in the pressure of the air also affect the boiling-point of water.

EXPERIMENT 17. To find whether the pressure of the air influences the temperature at which water boils. Attach a distilling flask *A* to the side tube of a second distilling flask *B* by a well-fitting india-rubber cork, place water in *B* and fit a thermometer to its neck as shown in Fig. 11; connect *C* to a filter pump*, place *A* in

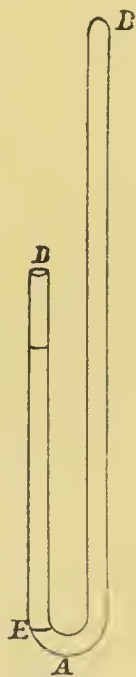


Fig. 10.

* An ordinary air-pump should not be used for this experiment as water will interfere with its action. A water-pump can be purchased for a few shillings, is easily fixed, and will give good results where there is a supply of water at a fairly good pressure.

a basin of cold water, start the pump and apply heat to *B*. When the water boils, note the temperature of its vapour. You will find it to be considerably below 100° . Next readmit air to *B*. When you do this the boiling-point of the water will rise until it once more reaches 100° . On the other hand, if you could force air into the apparatus you would raise the boiling-point of the water, but this cannot be done safely.

Another illustration of the influence of atmospheric pressure on boiling-point is to be found in the fact that water boils below 100° on a mountain top, where the pressure is lower than in the valleys,

so that the height of a mountain can be calculated from the temperature at which water will boil upon it, provided that the height of the barometer at sea level is known at the time of making the observation.

Returning now to the question asked above, we may conclude that there is a common cause for the changes in the height of the barometer, and in the boiling-point of water; both phenomena may be accounted for by changes

in the pressure of the atmosphere, and may be used to measure those changes.

22. The necessary precautions in taking a boiling-point.

From the results of the last two experiments it appears that a boiling-point must be taken when the barometer stands at a particular height—760 mm. is selected—or be corrected if it be taken at any other than the standard pressure. It is better to immerse the bulb of the thermometer in the vapour of the boiling liquid (see Fig. 11) rather than in the liquid itself. Finally the mercury in the capillary tube should be surrounded by the vapour as completely as possible in order that the whole of it may be heated.

23. The vapour pressure of water. We all know that water does not evaporate only at a boiling heat—puddles dry up. and a wet

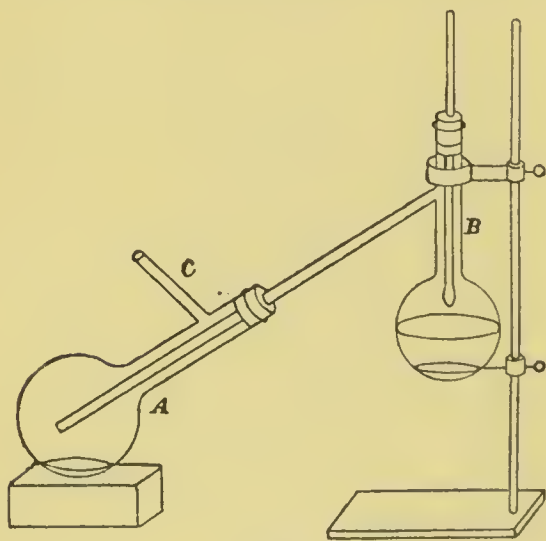


Fig. 11.

floor soon becomes dry even on a cold day. These and similar facts long ago led John Dalton to attempt to measure the pressure of water vapour at temperatures below its boiling-point, by introducing it into the empty space above the mercury in a barometer.

EXPERIMENT 18. To study the pressure of the vapour of water by Dalton's method (Fig. 12). Fill a tube *A* 1 metre long, 1 to 1.5 cm. in diameter, and closed at one end, with mercury, removing air bubbles as previously described. Close its open end with the thumb, immerse it in a basin of mercury *E*, and remove the thumb. A column of mercury about 760 mm. in height will remain in *A*. Mark its position, with gummed paper; suck some water into a pipette *C*, insert the tip of *C* under the mercury into the mouth of *A*, and blow two or three drops of water into *A*, taking care not to admit any air. Mark the new level to which the mercury falls, *A'*. The difference between the level *A'* and the former level corresponds to the pressure of the vapour of water at the temperature at which the experiment is made.

Attach a larger tube *G* by a cork *F* to the top of *A*, and pour some warm water into it. Notice that the mercury falls still further in *A*, showing that the vapour pressure of water increases with temperature. You will now see that you can measure the vapour pressure of a liquid at any temperature by filling *G* with water at that temperature and observing the effect produced.

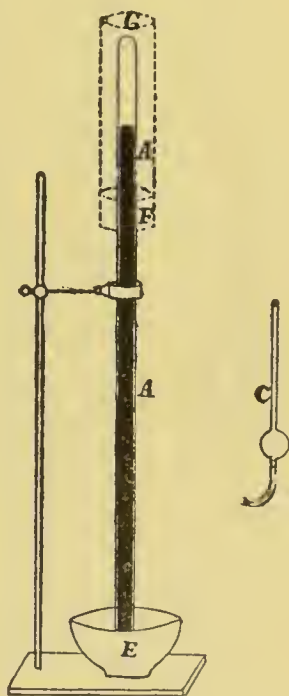


Fig. 12.

24. Relation of vapour pressure to boiling-point.

EXPERIMENT 19. To measure the vapour pressure of water at its boiling-point. Obtain a glass tube 2 or 3 mm. in diameter, 30 cm. in length, bent in the form shown in Fig. 13, and closed at *A*. Warm the tube gently to remove adherent air, fill the arm *A* with recently boiled water, introduce mercury into *B*, and invert the tube so that mercury may replace most of the water in *A*. Remove as much mercury as may be necessary so that it may stand at *C* in the arm *B*, and allow the apparatus to stand upright for a minute or so.

The tube should now contain a short column of water confined at *A* by the mercury below it. Heat some water in a good sized flask with a wide neck. When the water boils *freely* lower the little instrument gradually into the steam, and observe what happens. From your observations you will be able to state whether the vapour pressure of water at 100° , its boiling-point, is equal to the pressure of the air, or greater or less than this.

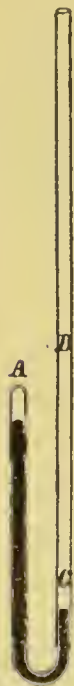


Fig. 13.

Question. If a very small quantity of a liquid were given to you, how would you find its boiling-point?

25. Physical constants. Physical qualities which can be measured and stated quantitatively, such as melting-points, boiling-points, &c., are called *physical constants*. They afford us a most useful and comparatively simple means of recognizing substances and of testing their purity.

When we prepared distilled water (8) we observed that the temperature of the steam remained at 100° as long as we continued to heat the water, and if the experiment were repeated upon any other single volatile substance, a similar result would be obtained. Thus, in the case of alcohol, the whole, or nearly the whole, would distil at about 78° . Let us now study the behaviour of a mixture of spirit and water.

EXPERIMENT 20. To study the behaviour of a mixture of spirit and water when it is distilled. Heat a mixture of equal volumes of rectified spirit and water in *A* (Fig. 6, p. 8) by means of a sand or water bath*.

As soon as boiling sets in read the thermometer. Notice that it stands at about 80° at first, but rises, first slowly, then more rapidly. As soon as the temperature reaches 90° change the receiver, and when the thermometer marks about 98° stop the experiment.

26. Fractional distillation. From the last experiment we learn that a mixture of two volatile substances differs from a single substance (or that an impure substance differs from a pure one) in

* When strong spirit, ether, benzene or any other very volatile and inflammable liquid is to be distilled, the vessel containing it should be heated by a water bath, that is, in a saucepan of water heated by a flame. When the temperature required is higher than 100° , as for distilling turpentine, an empty saucepan or a saucepan containing heated oil may be used.

this respect, that the former has no fixed boiling-point, but distils at gradually increasing temperatures which lie between fixed limits, depending on the nature of the mixture. If you taste a *drop* of the contents of each receiver, you will find that the part which distilled first stings like spirit, whilst the last fraction tastes like distilled water, which shows that most of the spirit is in the first fraction, and that the last fraction contains little or nothing but water. But even the first fraction did not, as you will have noticed, come over at exactly the boiling-point of spirit (78°), nor did it all distil at the same temperature, for it is not pure spirit, but still contains water. We might obtain a still stronger spirit by repeating the above process, but even then we should not get *absolute alcohol*, as pure spirit of wine is called, because water and spirit cling together so persistently that we cannot remove all the water in this way.

Fractional distillation is very largely employed by chemists, and we shall meet with other examples of its use.

27. Destructive distillation.

Although many liquids and solids

are volatile and may be distilled, they are not all volatile. Thus, for example, the fixed oils, such as linseed oil, olive oil, almond oil, lard, paraffin and wax, cannot be distilled unaltered.

EXPERIMENT 21. Heat a little sweet oil in a small retort *A* (Fig. 14). Collect the distillate in *B*, and compare it with the original oil. You will perceive that the oil has not distilled unaltered, for the distillate is semi-solid and has an acrid odour. It is a mixture of the products of a *destructive distillation* (see also carbon (Expt. 209), and coal gas, 303).

28. Density and relative density. If we place a drop of oil and a globule of mercury in some water, we shall find that the oil will float and the mercury sink, for the former is lighter and the latter

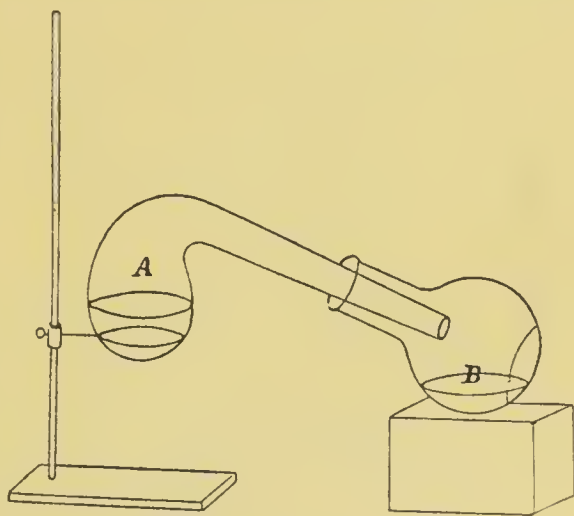
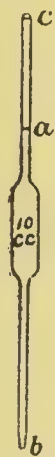


Fig. 14.

is heavier than water, or, as a physicist would say, the *density* of water is less than that of mercury, but greater than that of oil.

Let us compare the masses of equal volumes of these three substances more exactly, beginning with water.

EXPERIMENT 22. To compare the densities of some liquids. Fill a 10 c.c. pipette (Fig. 15) with distilled water to the mark *a* by dipping its end *b* into a vessel of water, sucking the water above *a*, quickly closing the end *c* with the forefinger, and then allowing the water to escape slowly at *b* till the lowest part of the curved surface * of the water is at *a*. If a drop of water should remain hanging at *b*, remove it, and let the water flow from the pipette into a beaker or flask of known weight. Then find the combined weight of the beaker and water, and calculate the weight of the water alone, setting out your results in your note-book in such a form as the following. It is a good plan to prepare the form in advance.



Weight of beaker and 10 c.c. of water	=	30.58	grams
" " " only	=	20.64	"
Weight of 10 c.c. of water	=	9.94	"

Repeat the experiment, using rain-water, and take the mean of the two results. You should find that 1 c.c. of water weighs very nearly 1 gram†.

Next perform a similar experiment, using quicksilver. It is a little difficult to keep quicksilver in the pipette, but if a 1 c.c. pipette be used to measure out the mercury, the manipulation will become a little easier, as the pipette can then be filled by plunging it to the mark into a basin of quicksilver and closing *b* with a finger.

Make a similar experiment with oil of almonds, and draw up a table of results such as that which follows. You will find that equal volumes of different liquids may contain very different quantities of matter or, as we say, have different *densities*.

Table of Results.

One c.c. of water weighs 0.994 gram (the weight at 4° is 1.0 grams).
 One c.c. of mercury weighs about 13.55 grams (see 29).
 One c.c. of almond oil weighs 0.90 gram.

* This surface is called a *meniscus*.

† The pipette will only deliver equal volumes of water if the water be at the same temperature when the two experiments are made.

The experiments made with rain-water and distilled water showed us that the weight of 1 c.c. of pure water is independent of the source of the water. This is true also of other definite substances, such as quicksilver and pure spirit of wine; hence the densities of substances afford us another set of 'physical constants' by which we can recognize them, and distinguish pure from impure specimens.

It is usual to state the densities of solids and liquids by numbers which express their relations to a standard, the standard being the density of water taken as unity*.

Thus the density, often called the *relative density*, of a solid or liquid gives us the ratio of the weight of 1 c.c. of that substance compared to the weight of 1 c.c. of water at 4°, and it can be found by dividing the weight of a given volume of the substance by the weight of an equal volume of water.

Thus, for example, we have found that 10 c.c. of mercury weigh 135.5 grams, and that 10 c.c. of water weigh 9.94 grams.

Then since $\frac{135.5}{9.94} = 13.7$, 13.7 is the density of mercury (the true value is 13.59).

Again, since 10 c.c. of almond oil weigh 9.0 grams, and since $\frac{9.0}{9.94} = 0.90$, 0.90 is the density of almond oil.

- Problems.* 1. If 50 c.c. of methylated spirit weigh 40.8 grams, find its density.
 2. If 5 c.c. of oil of turpentine weigh 4.3 grams, find its density.
 3. If the density of strong sulphuric acid be 1.85, find the weight of 500 c.c. of the acid.
 4. Find the weight of 15 c.c. of almond oil from its density, 0.90.
 5. If 10 c.c. of another sample of almond oil weighs 8.99 grams, what is its density?

The density of a liquid or solid may be defined as *the mass of unit volume of that substance expressed in terms of the mass of unit volume of water*. Thus when we say the density of a given substance is 2, we mean that the mass of unit volume, say of 1 c.c., of the substance is twice as great as the mass of unit volume of water. Hence, to find the density of a substance we have only to find the mass of 1 c.c. of it.

More exact methods for determining the densities, or specific gravities, of liquids will be found in works on physics.

* Water at 4° is usually taken. The reason for this will appear later.

29. Influence of temperature on density. All of us have seen the mercury rise and fall in a thermometer when it is heated or cooled, and therefore we can easily understand that 1 c.c. of warm mercury must contain less mercury, and therefore weigh less, than 1 c.c. of cold mercury. As other substances behave similarly we must always compare the densities of substances at similar temperatures.

From what has just been said it is evident that each substance* must have a different density for every degree and every subdivision of a degree of temperature. It is not, however, necessary to measure all these densities by separate experiments; if we find the value by experiment in a certain number of cases we can ascertain the others by the *method of interpolation*.

EXPERIMENT 23. To find the density of rectified spirit at different temperatures. Immerse a flask containing rectified spirit in a basin containing ice and water; when the temperature of the alcohol has fallen to 0° rinse a 10 c.c. pipette repeatedly with portions of it, and, when the pipette is well cooled, introduce 10 c.c. of it into a clean and dry *stoppered* flask of known weight; let the flask stand in the air till dew no longer remains upon it, dry and reweigh it; then from the weight of 10 c.c. of alcohol calculate its density.

Repeat the above experiment, using alcohol at 10° , 20° , and 30° , and calculate its density at these temperatures†.

Let us suppose that the spirit contained 70% of absolute alcohol: then the results should not differ very widely from the following:—

<i>Temperature.</i>	<i>Weight of 10 c.c. alcohol.</i>	<i>Density of alcohol.</i>
0°	8.84 grams	0.884
10°	8.76 „	0.876
20°	8.67 „	0.867
30°	8.59 „	0.859

30. To plot a curve. Obtain a piece of squared paper (Fig. 16) and mark, at equal intervals, along the line *AB*, a scale of temperatures from 0° to 50° . Next mark upon the line *AC* a scale of densities to suit your results, as that in Fig. 16 suits the figures in the third column of the above table.

Now mark on the paper, as in the diagram at *C* and *x, x, x*, the points

* See Preface, p. viii.

† If a class is working its members should divide the work among them.

at which lines parallel to AC drawn from the respective temperatures meet lines parallel to AB drawn from the corresponding densities. Join the points C and x, x, x , by a line CD .

With the aid of this diagram you can ascertain the density of the alcohol used in your experiments at any temperature between 0° and 30° . Let us suppose that you wish to know its density at 15° .

Follow the line starting from 15° on AB till it cuts CD at g .

Draw a line from g , parallel to AB , to meet AC . It does so at 0.871.

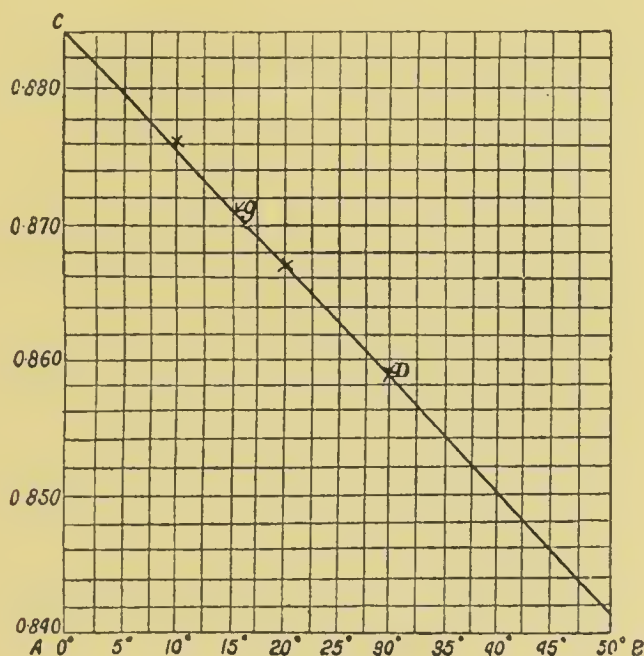


Fig. 16.

Then the density of the alcohol at 15° is 0.871. By continuing the line CD towards B we should obtain the necessary data for finding densities at temperatures above 30° , but this would not be quite trustworthy, for we have no actual measurements to guide us at these higher temperatures, and the character of the curve might possibly change above 30° .

Problems. With the aid of Fig. 16 find :—

1. The volume of 1 gram of alcohol at 25° .
2. The temperature at which alcohol has the density 0.861.
3. The size of the bottle required to hold 800 grams of alcohol at 15° .

Influence of temperature on the density of water. Alcohol

was used for Experiment 23, because it expands more rapidly than water, and therefore small experimental errors were comparatively unimportant. The behaviour of water under changes of temperature is, however, both interesting and important.

EXPERIMENT 24. To learn how the volume occupied by a given mass of water is affected by changes of temperature. Fit a long narrow glass tube *B* (Fig. 17) to a flask *A* of about 250 c.c. capacity; fill the flask to the brim with water, and place the cork in position, forcing it well home, so that some water enters the narrow tube.

Now place the flask of water above a Bunsen burner and observe what happens. When you have discovered whether water expands or contracts when heated, immerse the flask in a mixture of ice and water, and observe the effect of cooling it. You will find that at first the water will fall in *B*, but that presently it will rise again, for there is a temperature, viz. 4° , at which water expands both when it is heated and when it is cooled. This is called its temperature of *maximum density*.



Fig. 17.

If similar experiments are made with mercury, oil, and other liquids, they will be found to contract regularly when cooled, for water alone behaves in the peculiar manner described above*. This is fortunate for mankind, as you will understand if you consider what must happen to the water of a pond or lake when the temperature of the air falls below the freezing-point. At first, of course, as the surface of the pond cools, the upper layers of water increase in density and therefore sink and mingle with the warmer water below until the temperature of the whole has fallen to 4° . After this any further cooling causes the upper layer of water to expand, consequently the coldest water no longer sinks, but floats on the surface, is rapidly cooled to 0° and then frozen. During this latter stage the water at the bottom of the pond loses but little heat, and though long continued cold may cause the gradual formation of a thick crust of ice upon its surface, the great bulk of the water will remain at 4° , except in the case of shallow water or in the regions of very severe cold. Now if water contracted regularly like other liquids, no protecting layer would be formed during a frost, but the cooled water would continue to

* Since this was written a similar phenomenon is said to have been observed in the case of iron.

sink and the warmer to rise, until the whole had fallen to 0° , when freezing would set in. Then, if the ice sank, not only would the fish probably be destroyed, but the summer's heat might be insufficient to thaw the ice formed in winter, and thus a large part of the earth might be reduced to a condition resembling that of the arctic regions.

The relative densities of solid and liquid water. Since ice floats on water it must be less dense than water. It follows also that water expands when it freezes, and that ice and snow contract when they melt.

The expansion of water on freezing can easily be observed by placing a corked flask filled with water at 0° C. in a freezing mixture made by mixing ice and salt. If the flask is well covered by the freezing mixture a very rapid expansion will occur and the flask will be found to be broken at the end of the experiment. The force with which the water expands is indeed so great that a well-secured cast-iron bottle can be broken in a similar manner, and it is generally agreed that the freezing of water contributes to the gradual disintegration of the rocks on the surface of the earth. When water collected in their crevices is frozen in winter its expansion, gradually or suddenly, as the case may be, enlarges their crevices and ultimately breaks them to pieces.

31. To determine the specific gravity of a solid. The specific gravities or relative densities of solids, like those of liquids, are usually stated with reference to the density of water. Thus a cubic centimetre of platinum weighs 21.5 grams, whilst a cubic centimetre of water weighs 1 gram. Therefore the specific gravity of platinum is 21.5. It will be seen that the specific gravity of a solid expresses the weight in grams of one cubic centimetre of that solid.

To find the specific gravity of a solid we must find its weight and volume and divide the former by the weight of an equal volume of water. Thus the specific gravity of a solid

$$= \frac{\text{The weight of the substance}}{\text{The weight of an equal volume of water}}.$$

Now it has long been known that when a substance is first weighed in air and then in water the difference between the two weights gives us the weight of a volume of water equal to the volume of the solid. Verify this by tying a glass stopper to a fine thread and suspending it from one arm of a balance. Place weights on the pan of the scales to balance the stopper. Then immerse the stopper in a graduated cylinder

containing a known volume of water. Note the new position of the water in the cylinder and calculate the volume of the stopper.

On putting the balance into action you will find the stopper weighs less than before; reweigh it and determine the loss of weight. If your work is correctly done you will find the loss of weight is equal to the weight of the water displaced.

We can therefore find the specific gravity of a solid by weighing it first in air and then in water. Thus :—

$$\frac{\text{The weight of solid in air}}{\text{Loss of weight of solid in water}} = \text{specific gravity.}$$

Solids soluble in water may often be weighed in other liquids.

There are various special ways of taking the densities of solids, but these must be sought in works on practical physics. In case the student does not work in a physical laboratory he will do well to determine the specific gravity of a few substances such as glass, lead and tin, by the method just described.

CHAPTER IV

SOLUTIONS, LIQUID DIFFUSION AND CRYSTALS

32. Solutions of solids in liquids. We have learnt that most natural waters contain a good deal of solid matter in solution which can be recovered by evaporating the water (7), and we all know that sugar and many other things dissolve readily in water. Water, however, is by no means the only liquid which acts as a solvent; many substances which refuse to dissolve in water do so quite freely in other liquids. We must now examine the behaviour of a few other solvents, and then study the phenomena of solution in water more fully; but first the student must acquaint himself with two useful operations by which solids may be separated from liquids.

EXPERIMENT 25. To separate a solid from a liquid (a) by decanting, (b) by filtering or straining. Mix some chalk and water.

(a) *Decanting.* Allow some of the mixture to stand in a deep vessel, such as a test tube. The solid will soon fall as a sediment to the bottom of the tube, whilst the water will float above it. Decant the latter into a basin or flask, using a glass rod to direct its flow as shown in Fig. 18.

(b) *Filtering.* Fold a piece of filtering paper about eight inches square, twice, as shown in Fig. 19, then cut off the open edges along the dotted line *a a*, and open the paper so that it forms a hollow cone.



Fig. 18.

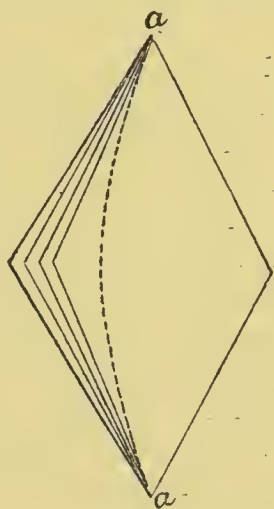


Fig. 19.

Place this, tip downwards, in a funnel, moisten it with water, place the narrow end of the funnel in the mouth of a flask, and pour the rest of the mixture into the paper cone. The water will pass into the flask, whilst the chalk will remain on the filter.

Linen or flannel is sometimes used for filters instead of paper, and substances which destroy these may be strained through plugs of glass-wool, or asbestos, placed in the neck of a funnel.

EXPERIMENT 26. To find a solvent for sulphur. Powder some roll sulphur, and shake small portions of the powder in test tubes containing water, methylated spirit, and carbon disulphide. Decant or filter the liquids separately into three dishes and evaporate them. As the two last-mentioned liquids are very inflammable, evaporate them on a *water bath*, and do not allow them to come near a flame*.

You will find that the sulphur is dissolved only by the carbon disulphide.

Exercises. 1. Try, by similar experiments, to dissolve small fragments of iodine in water and chloroform respectively.

2. Try to find a solvent for beeswax.

3. Try to find a solvent for chalk.

4. Try to find a solvent for iron rust.

* Carbon disulphide must be evaporated in a fume closet.

In case you fail to find solvents for chalk and iron rust, try the action of hydrochloric acid moderately diluted with water, and evaporate the solution obtained in a fume closet or in the open air, as acid fumes are unwholesome. Compare what is left with the substance taken. For example, look at it closely to see if it is altered, and try if it will now dissolve in water.

If you carefully consider the results of the above series of experiments, you will find you have discovered:—

(1) That water is not a universal solvent, but that other solvents are available when water fails us.

(2) That the solutions of iodine, sulphur, and wax yield up iodine, sulphur, and wax unaltered when they are evaporated. But that solutions of chalk and iron rust in hydrochloric acid yield residues which are quite unlike chalk and iron rust in appearance, and which are readily soluble in cold water. In short, that hydrochloric acid does not merely dissolve chalk and iron rust, but alters them, producing something *new*.

Therefore it is evident that solvents are of two kinds:—

(a) Those from which the original substances can be recovered by evaporation.

(b) Those from which the original substances cannot be so recovered, but which change the substances dissolved, producing something with a new set of properties.

33. Influence of temperature on the solubility of solids in water. EXPERIMENT 27. To study the influence of temperature on the solubility of chlorate of potash, common salt, and of sodium sulphate in water. (1) Add powdered chlorate of potassium little by little to 50 c.c. of cold water in a flask, shaking well, until no more will dissolve. Heat the contents of the flask and add more of the salt. When no more will dissolve, decant, and cool some of the clear solution, by plunging the flask containing it in cold water, and describe your results.

(2) Repeat the above experiment, using common salt, and describe the results obtained, as before.

(3) Place a few grams of sulphate of sodium in a test tube with about one-tenth as much water. Warm the contents in the test tube cautiously to 34° . When no more salt will dissolve, decant some of the solution and heat it more strongly, observe what happens, and write an account of your observations. If you follow these instructions carefully you will find:—

1. That chlorate of potash is much more soluble in hot water than in cold.

2. That common salt is about equally soluble in hot and cold water.

3. That sodium sulphate is more soluble at 34° than at higher temperatures.

From these results it appears that the solubility of a salt in water may be greater at high temperatures than at lower; that it may be unaffected by the temperature of the liquid employed; and, finally, that it may be less in hot water than in cold.

34. Solubility curves. The influence of temperature on the solubility of a solid can be very conveniently expressed by means of a curve, similar to that which was employed (Fig. 16) to show the influence of temperature on the density of alcohol.

EXPERIMENT 28. To construct solubility curves for common salt, potassium chlorate, and sodium sulphate. Find how much of each salt will dissolve in 100 parts of water, at 0° , 20° , 40° and 60° , employing the method described below. Then mark your results on squared paper as before, and compare them with the curves in Fig. 20.

As it would take a single student a long time to make so many determinations it will be wise to divide the work; one student finding the solubility of common salt at 0° and 20° , another at 40° and 60° , and so on. The workers will then find it interesting to see whose results agree best with the curves given in the figure.

Method. Find the weight of a small basin provided with a short glass stirring-rod. Obtain also a small stoppered bottle of known weight. Place a flask containing 40 or 50 c.c. of water in a water bath kept at 0° , 20° , 40° , or 60° as the case may be, and add the finely powdered salt gradually, shaking well, until excess is present. Agitate the excess of salt with the liquid for ten or fifteen minutes, taking care to keep the water bath at as nearly as possible the desired temperature. Then allow the excess of salt to settle, quickly decant about 5 c.c. of the clear solution into the weighed bottle, allow it to cool [why?] and weigh it. Transfer the solution with any crystals that may have formed to the evaporating basin, taking care to convey every trace of salt into the basin by repeatedly rinsing the bottle with warm water. Evaporate the solution on a water bath, or in a drying oven, with frequent stirring to break up the crystals and prevent them from entrapping small drops of water, cool the dried salt in a *desiccator* (see Fig. 21) and weigh the dish and its contents. It is a good plan

to reheat the dish and salt and reweigh them in order to assure yourself that all the water has been expelled.

Example of a statement of results :—

A.	Weight of bottle and solution taken . . .	= 25.55 grams
	Weight of bottle alone	= 19.25 „
	Solution taken	= <u>6.30</u> „
B.	Weight of dish, rod, and dry salt . . .	= 18.60 grams
	„ „ and rod alone	= 17.55 „
	Weight of salt from 6.30 grams of solution =	<u>1.05</u> „

The solubility of a solid at a given temperature is usually defined as the amount of the solid dissolved by 100 grams of the solvent at that temperature.

From the above figures we see that 1.05 grams of salt were dissolved by $6.30 - 1.05 = 5.25$ of water.

5.25 grams of water dissolve 1.05 of salt ;

∴ 1.0 gram „ „ dissolves $\frac{1.05}{5.25}$ „

And 100 grams „ „ dissolve $\frac{1.05}{5.25} \times 100 = 20$ of salt.

The curves in Fig. 20 show the solubility of the three salts mentioned in water at various temperatures.

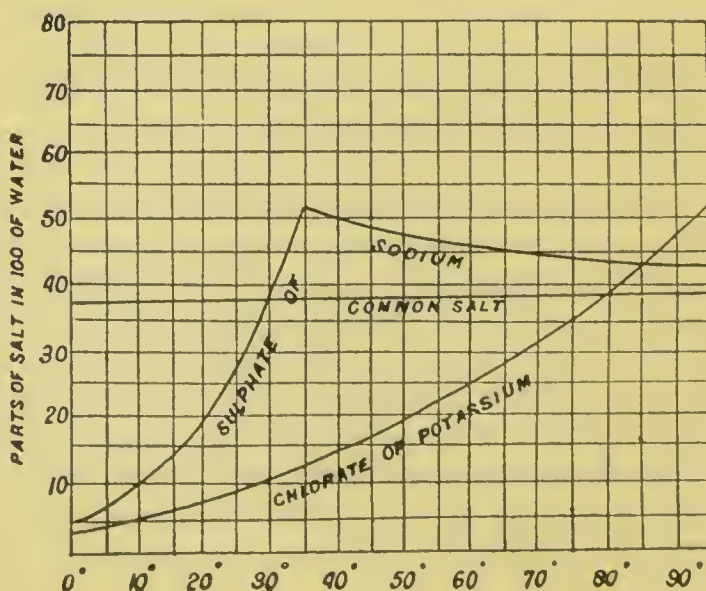


Fig. 20.

The majority of salts are more soluble in hot water than in cold, like potassium chlorate. Common salt is somewhat singular, for it is nearly equally soluble at all temperatures. A few salts, like sulphate of sodium, are less soluble in hot water than in cold or moderately warm water. A further account of this subject will be found in 332.

Note I to Experiment 28. Another method of preparing a *saturated* solution of a salt at a given temperature, consists in making a nearly saturated solution at a higher temperature than the required one, cooling the solution to the desired temperature, and then adding a few crystals to start crystallization. After shaking the liquid for a minute or two with the crystals which form, the solution may be decanted as before. Care must be taken that the solution is decanted at the required temperature, as the crystallizing of the salt may be accompanied by rise of temperature (14).

Note II—Desiccators. It is not possible to weigh anything correctly whilst hot (Appendix, p. 492, 3), and if a salt be allowed to cool in the air water may be absorbed; to prevent this it must be cooled in dry air. Fig. 21 represents an inexpensive form of desiccator. Sulphuric acid, or some other drying agent, is placed in *A*, the object to be cooled at *B*, and the whole is closed by a glass lid *C* ground to fit the mouth of the desiccator, the joint being made air-tight by grease.

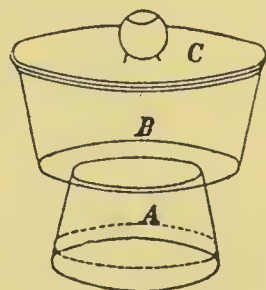


Fig. 21.

35. Liquid diffusion. Place some water, coloured with blue litmus, in a deep cylinder. Place a layer of strong hydrochloric acid beneath it, without disturbing the supernatant liquid, by means of a pipette. Mark the line where the two liquids meet, and set the apparatus where it may remain undisturbed, and at as uniform a temperature as possible. If you observe the line of junction of the two liquids from time to time, you will discover that the acid gradually rises and mingles with the lighter layer above it. In the course of time the acid will spread itself equally throughout the contents of the cylinder. This is due to *liquid diffusion*, and shows us that though a liquid may, as a whole, remain apparently motionless, yet its particles are in a state of active movement.

The diffusive powers of various substances in solution were first carefully compared by Graham. He placed 700 c.c. of water in a

cylinder, introduced very gently, by means of a pipette provided with a very fine delivery tube, 100 c.c. of the liquid to be examined, then placed the apparatus aside for a definite period, and afterwards carefully syphoned off the liquid in equal fractions, beginning with the top layer. He then ascertained what amount of the substance under investigation was present in each fraction.

The following table gives the 'times of equal diffusion' for some of the substances examined:—

Hydrochloric acid	.	.	.	.	1	
Common salt	.	.	.	.	2.3	
Sugar	.	.	.	.	7	
Sulphate of magnesium	.	.	.	.	7	
Albumen (from eggs)	.	.	.	.	49	} Colloid or glue-like substances.
Caramel	.	.	.	.	98	

On comparing the figures in this table we observe a marked difference between the behaviour of crystalline substances such as sugar, and that of non-crystalline or colloid substances such as albumen or caramel (for dialysis see 309: for osmotic diffusion, 335).

CRYSTALS.

36. Modes of obtaining crystals. Whilst making the preceding experiments, the student will have observed that some hot solutions deposit particles of salt during cooling, which are more or less regular in form, and which reflect light; these are called *crystals*. Crystals are usually obtained either by cooling or evaporating a solution of a solid, by solidifying the previously fused substance, or by condensing the vapour of a volatile solid.

EXPERIMENT 29. To prepare crystals of copper sulphate and other substances from their solutions in water or acid.

1. Heat about 200 c.c. of water to 70° in a flask, add powdered sulphate of copper gradually until no more will dissolve, heat the solution to near the boiling-point [what is the object of this?], filter it quickly into a basin, and allow it to cool. Before long a crop of crystals will form. Notice how closely the more perfect crystals resemble each other, and preserve some of the finest.

2. Prepare crystals of bichromate of potassium in a similar manner.

3. Dissolve some iron filings in 10 c.c. of sulphuric acid diluted with 40 c.c. of water, filter the solution from the black residue, which consists partly of black lead or graphite (275). Evaporate the

solution, and leave it to cool and crystallize. Notice that in this case the product differs from the materials from which it was made. It is sulphate of iron.

4. Examine the action of zinc on dilute sulphuric acid, and preserve the product, which is sulphate of zinc.

EXPERIMENT 30. To crystallize sulphur by cooling melted sulphur. Heat some lumps of sulphur in a porcelain crucible or small iron pot, supported on a tripod stand, by means of a Bunsen burner (Fig. 4), adding more sulphur as it fuses till the crucible is nearly full, and then remove the burner. As soon as a solid crust has formed on the sulphur, make two holes through this, as far apart as possible, seize the crucible with a pair of tongs, and pour out the remaining liquid sulphur through one of the holes. Then gently remove the crust, and you will find a mass of beautiful amber-coloured needles of *prismatic sulphur* (Fig. 22 *a*). Several of the metals may be crystallized by this method.

Let us next ascertain whether sulphur is deposited from solution in carbon disulphide (see Expt. 26) in the same form.

EXPERIMENT 31. To compare crystals of sulphur made in different ways. Dissolve about 10 grams of

sulphur in a little cold carbon disulphide, filter the solution into a small flask, plug the mouth of the flask with cotton-wool, and place it in an empty desiccator loosely covered that the carbon disulphide may escape slowly. In a few days crystals will appear. Examine them to see whether they are prisms (Fig. 22 *a*) or octahedra (Fig. 22 *b*).

EXPERIMENT 32. To obtain crystals by condensing the vapours of volatile solids. Heat some iodine gently in a small dry test tube or flask, taking care to keep the upper part of the vessel cool. Notice that the iodine *sublimes*, i.e. disappears from the hotter parts of the tube and recondenses in crystals on the cooler parts.

Heat a *minute* fragment of arsenic* in a tube of hard glass very gradually, by bringing the bottom of the tube first near and then very slowly into a flame, and examine the sublimate with a lens. You will find it largely consists of minute, brilliant octahedral crystals.

* Do not touch this with your hand.

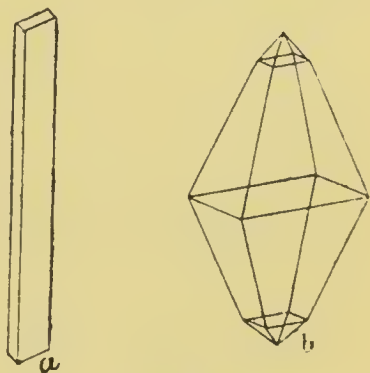


Fig. 22.

Make a similar experiment with iodide of mercury, and write an exact account of your observations, drawing pictures of the various crystals obtained, if you can do so.

Many solid substances besides copper sulphate, iron sulphate, arsenic, &c., can assume definite geometrical forms under favourable conditions. Such substances are said to form *crystals*. It is not easy to obtain perfect crystals, and often they are so small that we can only recognize them with the aid of a lens. True crystals or fragments of crystals may often be distinguished from imitation crystals, cut for example from glass, by their appearance when broken. A piece of glass will split up equally well in all directions, and its fragments are usually very irregular in form, and exhibit conchoidal or shell-like surfaces. But crystals exhibit what is called *cleavage*—they tend to split more easily in some directions than in others. If you obtain a crystal of *selenite*, or of calc-spar, and either break it cautiously in a mortar, or split it up with a penknife, and compare the fragments with a piece of broken glass, you will readily recognize the difference between a crystal and a vitreous substance.

37. Purifying substances by crystallizing them. We have learnt how use may be made of the unequal volatility of substances, when we wish to separate them from each other, by the process of 'fractional distillation' (26). Their varying behaviour with solvents can be employed in a similar manner.

EXPERIMENT 33. To separate gunpowder into its component parts. The old-fashioned gunpowder is a mixture of sulphur and carbon with a salt called nitre. Sulphur dissolves in carbon disulphide, but carbon and nitre do not, therefore we can extract the sulphur from gunpowder by means of this solvent. Again, water dissolves nitre but does not dissolve either carbon or sulphur. Hence nitre can be extracted from either of these by water.

Weigh into a flask two or three grams of gunpowder, add some carbon disulphide, digest them for a little while, and pour the solvent through a filter into a dish. Repeat the treatment, using fresh carbon disulphide, two or three times. Then evaporate the mixed filtrates on a water bath and weigh the sulphur obtained. Dry the residue left by the carbon disulphide, extract the nitre in a similar manner by means of warm water, evaporate the solution and weigh the nitre. Dry and weigh the carbon which remains; add together the respective weights of the three components. Their sum should not differ greatly from the weight of the gunpowder taken.

EXPERIMENT 34. To purify a salt by crystallizing it from water. Add a drop or two of a solution of silver nitrate to a few drops of a solution of nitre. If the nitre be pure you will not perceive any effect.

Make a similar experiment using common salt. A white solid precipitate of silver chloride will fall. This difference between nitre and common salt, which will be explained subsequently, gives us a means of detecting the latter in the presence of the former.

Now add 5 grams of common salt to 95 grams of nitre, dissolve the mixture in 50 c.c. of boiling water, and test a drop of the hot solution for chloride as before. Allow the solution to cool that crystals may form. Collect and drain these, and press them between blotting-paper to remove the *mother liquor*. Recrystallize them from solution in half their weight of boiling water, then drain and dry them, and again test them for common salt. You will find very little evidence of its presence. Finally, weigh the purified nitre. The results of this experiment teach us two things: (i) that one substance can be separated from another by crystallizing; (ii) that a great deal of the substance to be purified may be lost in the *mother liquor*.

38. How to grow crystals. In order to get good crystals certain precautions must be taken. The solution in which the crystals are grown must be saturated with the salt, and it must be kept at a nearly uniform temperature, for if it be allowed to cool quickly small crystals may form suddenly in large numbers, and, on the other hand, if its temperature should rise, the crystals in process of formation may be redissolved.

EXPERIMENT 35. To grow crystals of alum or of chrome alum. Add about half a kilogram of powdered alum to two or three litres of warm water, using rather more of the salt than the water will hold in solution at ordinary temperatures (that is, add the salt till the solution will deposit crystals on cooling), and filter the solution into a large jam-pot. Tie a small piece of glass rod to one end of a horse-hair, suspend it in the warm solution, and allow the latter to cool slowly. Crystals will soon be deposited, and probably one or more of them will be attached to the horsehair; if not, repeat the experiment.

When a well-shaped octahedron has formed on the horsehair, decant the cold solution into a clean vessel, reimmerse the hair with the attached crystal in the liquid. Set aside the whole in some place where its temperature will be fairly uniform, and inspect the crystal, or

crystals, and the other contents of the crystallizing vessel occasionally. If all go well the crystal will gradually increase, and with care and patience it may be grown to a considerable size.

If at any time small crystals form upon the larger one they must be removed, and any crystals which may form on the bottom or sides of the beaker should also be removed, otherwise they will grow as the solution evaporates, and retard the progress of the suspended crystal.

Crystals may also be grown lying on the bottom of a flat basin, provided they are kept at a uniform temperature in saturated solutions, and frequently turned so that they may develop equally on every side. Crystals of the three alums, of chromate of potassium, and of the sulphates of copper, zinc, and magnesium are all tolerably easy to grow.

Some curious effects may be obtained with the alums. These are isomorphous (338) and will therefore crystallize together. If a crystal of purple chrome alum is immersed in a solution of colourless common alum, it will continue to grow as if it were in its own solution, so that presently one has a crystal of the purple salt locked up inside an outer colourless crystal of similar form.

A further account of crystallography will be found in Chapter XXII.

CHAPTER V

COMPOUNDS, ELEMENTS, MIXTURES, AND CHEMICAL CHANGE

39. Composition of water. We have learnt that water boils at 100° , freezes at 0° , and has certain other definite physical properties: therefore it is not a mixture like the spirit of wine examined in Experiment 20. Let us now study its behaviour under the influence of agents, such, for example, as electricity.

If a constant supply of electricity is not available, you should obtain a battery of four Grove or Bunsen galvanic cells. A Grove cell consists of a pot *A* (Fig. 23) of glazed earthenware containing an unglazed pot *G*. In *G* is placed a sheet of platinum *D**, and between *A* and *G* is a sheet of zinc *B*, which has been moistened with dilute sulphuric acid and well rubbed with mercury. *G* is filled with strong nitric acid, and *A* with a mixture of 1 part of sulphuric acid with 12 of water. If the cell is long in action the latter cannot be used twice. You will observe,

* In a Bunsen cell a block of gas carbon replaces the platinum.

when you put the cell together, that the sulphuric acid does not act visibly on amalgamated zinc as it does on the unamalgamated metal. Two wires *W W* are joined to *D* and *B* respectively. If you bring together the ends of *W W* and then separate them you should see a minute spark at the moment of breaking contact. A current of electricity is supposed to flow through the wires when they are joined, and to travel as if it came from the carbon and passed to the zinc plate. When a current flows through a cell of any kind, the part at which it enters the cell is called the anode, and that at which it leaves the cell is called the kathode. They are often distinguished by the + and - signs respectively. To combine the four cells, connect the zinc plate of one cell to the platinum of another by a wire, then the zinc of the second to the platinum of a third, and so on, leaving free the wire from a platinum plate at one end of the battery, and the wire from a zinc plate at the other. If now you put *W W* into communication as before, you will obtain a larger spark on breaking contact, and if you introduce the ends of *W W* into some water slightly acidulated with sulphuric acid, you will see minute bubbles of gas rise from them. We must examine these bubbles carefully.

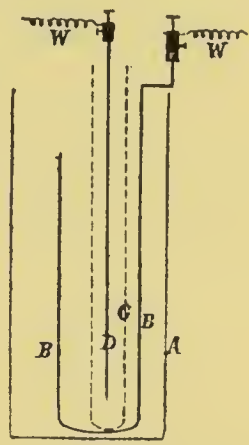


Fig. 23.

EXPERIMENT 36. To examine the action of electricity on water.

Attach the wires *W W* to two small sheets of platinum *a a'* (Fig. 24), suspended by platinum wires *R R* in a small bottle filled with dilute sulphuric acid, and provided with a *delivery tube B**. Notice that when you do this bubbles are

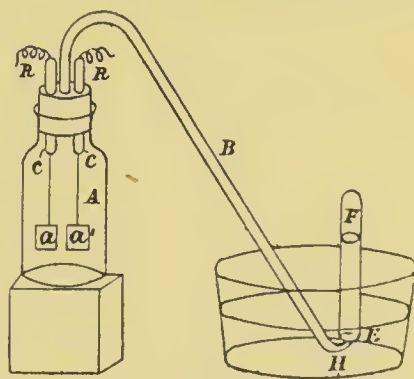


Fig. 24.

given off at *a a'*, which do not condense as they pass into the surrounding cold water, and which, therefore, cannot consist of steam.

Collect half a test tube full of the gas in *F*, close the mouth of *F*

* To make the wires fit the cork tightly they may be fused into pieces of glass *c c*.

with your thumb, remove it from the water, plunge a lighted taper into the gas, and notice that a violent explosion occurs, showing that the bubbles do not consist of atmospheric air, but of a new gas, or possibly of a mixture of two or more gases, for we have not yet examined what is given off at the two plates separately.

For this purpose obtain a wide-mouthed bottle *, cut off its bottom so as to form a kind of basin *B* of the top, as shown in Fig. 25, fit a cork *E*, carrying the two electrodes *d d'*, in its neck, fill *B* with dilute sulphuric acid to the level *a a'*, place two tubes *c c'*, also filled with dilute acid, above *d d'*, and connect *d d'* with the battery. When you have collected a good deal of the gas evolved, examine the

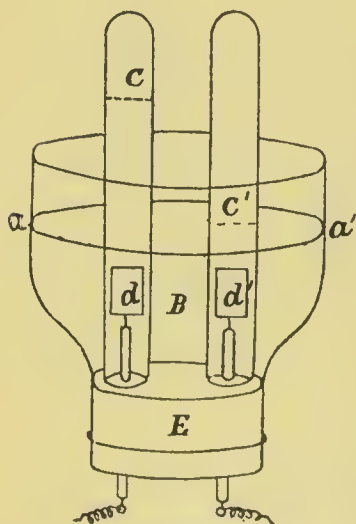


Fig. 25.

contents of the tubes, noting the volume and colour of the gas in each tube, and whether a flame will ignite it as before, also whether a glowing match-tip is extinguished or bursts into a fierce flame when it is plunged in the contents of each test tube.

From your observations you will discover that one tube *C* [was *d* connected with a zinc or with a platinum plate?] contains a colourless gas, which ignites glowing carbon, but does not burn, whilst the other contains about twice as much of a colourless gas, which burns itself, but does not ignite glowing carbon †. From these results it is evident that we have obtained not one new gas but two gases

from acidulated water by the action of electricity, but we do not yet know whether the two gases come from the water or from the acid or from both.

We have seen that when mixed they can be exploded by a spark. Let us attempt to find what was formed in the explosion; possibly the product may throw some light on this further question.

EXPERIMENT 37. To the bottle *A* of Fig. 24 attach the tube *CBD* (Fig. 26) in place of *B*. In *CBD* place a plug of asbestos about 3 cm. long and closely, but not too tightly packed, at *B*. At *D* place a column

* The apparatus described in 144, Fig. 65, may be used for this experiment if the carbon electrodes are replaced by sheets of platinum.

† As the two gases are slightly and *unequally* soluble in water it is a good plan to reject the first portions collected.

of rough iron filings 8 or 10 cm. long so that they fill the tube and lie closely, but will allow a gas to pass freely. At c' contract the tube and

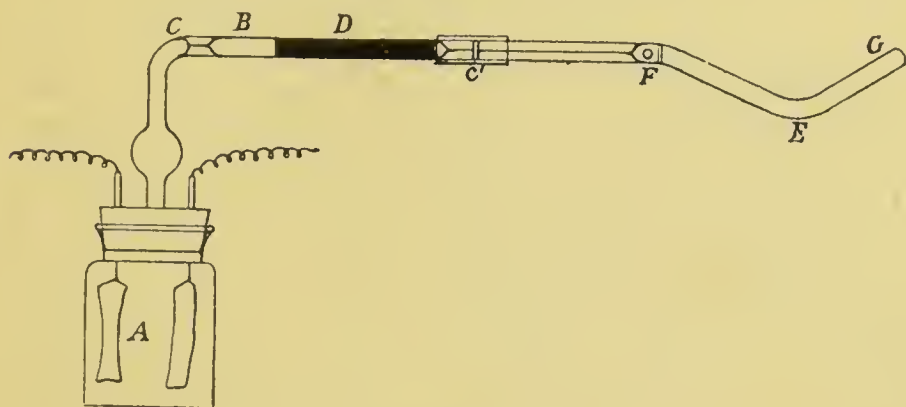


Fig. 26.

join to it another tube FG , also contracted near c' but about 5 mm. wide from F to G , by an india-rubber joint; push a fragment of platinized asbestos to the point F , and secure it with a short plug of ordinary asbestos. Start the action of the current, keeping A cool, and warm F very gently till the asbestos glows. Keep the tube cool at E , and test the liquid which gradually collects there to learn if it is water or acid*.

NOTE.—If the tube CBD is properly filled this experiment is quite safe and goes beautifully, but it should be prepared and fixed for the younger pupils, if they do the experiment. The platinized asbestos, if of good quality, will itself bring about combination, but often it is necessary to apply a little heat to it.

40. Elements and compounds. The results of the last experiment make it possible for the student to understand the use of the word *element* in chemistry, and the difference between elements and compounds.

We have seen that water can be split, by electricity, into two gases, each quite unlike water in its properties. Now a substance which can be thus broken up by such agents as heat and electricity is called

* The liquid could be shown to be water, if the experiment were made on a large scale, from its physical properties.

a *compound*, whilst substances which have never yet been resolved into simpler forms of matter are called *elements*. Let us consider another example :—Lavoisier found that when he heated 45 grains of oxide of mercury, they split into $41\frac{1}{2}$ grains of mercury and $3\frac{1}{2}$ grains of oxygen (4). That is to say, by the mere action of heat on a definite weight of one substance, he obtained a corresponding quantity of two entirely new substances. It follows that oxide of mercury is not an element or simple substance but a compound.

On the other hand, when mercury or the two gases obtained from water, oxygen and hydrogen, are submitted to the highest temperatures, or acted on by the strongest electric currents, or in any way similarly treated, they never show any signs of thus breaking up into simpler substances. Hydrogen, oxygen, and mercury are therefore termed *elements*. It may be that at some future time these three substances will be proved to be compounds, but until that occurs we regard them as *elements*.

An element, then, may be defined as *a substance which has not yet been resolved into simpler forms of matter* (see also 122).

A list of the chief elements, as far as we at present know them, is given in the table on page 47. There are, as you will see, seventy or more elements in all, but we know very little about some of them. In the second and third columns of the table are given the *symbols* and *combining numbers* of the elements, but these do not concern the student at present ; they are placed there for future convenience.

41. Distribution of the chief elements in nature. The known parts of the crust of the earth—the sea, the atmosphere, the rocks and their inhabitants—are chiefly composed of about fifteen elements. The rest occur in comparatively small quantities, but some of them are very widely spread.

42. Chemical compounds and mixtures. We have met with the elements oxygen and hydrogen in two distinct conditions. At the beginning of Experiment 37 we had them in the form of a mixture of two gases. When an electric spark was passed through this mixture, heat and light were given out, the gases disappeared and were replaced by water. Here we have an example of a *chemical change*. At the first stage the oxygen and hydrogen were merely mixed mechanically, each substance was still a colourless, tasteless, odourless gas ; the former could still support combustion, the latter was still combustible. But after the explosion the two gases were *combined*, or

TABLE OF ATOMIC WEIGHTS.

INTERNATIONAL ATOMIC WEIGHTS.

1904.

		O = 16.	H = 1.			O = 16.	H = 1.
<i>Aluminium</i>	Al	27.1	26.9	Neodymium . .	Nd	143.6	142.5
<i>Antimony</i>	Sb	120.2	119.3	Neon	Ne	20	19.9
(<i>Stibium</i>)				<i>Nickel</i>	Ni	58.7	58.3
Argon	A	39.9	39.6	NITROGEN . .	N	14.04	13.93
ARSENIC . . .	As	75.0	74.4	Osmium	Os	191	189.6
<i>Barium</i> . . .	Ba	137.4	136.4	OXYGEN . . .	O	16.00	15.83
<i>Bismuth</i> . .	Bi	208.5	206.9	Palladium . . .	Pd	106.5	105.7
BORON	B	11	10.9	PHOSPHORUS .	P	31.0	30.77
BROMINE . . .	Br	79.96	79.36	<i>Platinum</i> . . .	Pt	194.8	193.3
<i>Cadmium</i> . .	Cd	112.4	111.6	<i>Potassium</i> (<i>Ka-</i>	K	39.15	38.86
Caesium . . .	Cs	132.9	131.9	<i>lium</i>)			
<i>Calcium</i> . . .	Ca	40.1	39.8	Praseodymium .	Pr	140.5	139.4
CARBON	C	12.00	11.91	Radium	Rd	225	223.3
Cerium	Ce	140.25	139.2	Rhodium	Rh	103.0	102.2
CHLORINE . . .	Cl	35.45	35.18	Rubidium	Rb	85.4	84.8
<i>Chromium</i> . .	Cr	52.1	51.7	Ruthenium . . .	Ru	101.7	100.9
Cobalt	Co	59.0	58.56	Samarium	Sm	150	148.9
Columbium . .	Cb	94	93.3	Scandium	Sc	44.1	43.8
<i>Copper</i> (<i>Cu-</i>	Cu	63.6	63.1	Selenium	Se	79.2	78.6
<i>prum</i>)				SILICON	Si	28.4	28.2
Erbium	Er	166	164.8	<i>Silver</i> (<i>Argentum</i>)	Ag	107.93	107.12
FLUORINE . . .	F	19	18.9	<i>Sodium</i> (<i>Na-</i>	Na	23.05	22.88
Gadolinium . .	Gd	156	155	<i>trium</i>)			
Gallium	Ga	70	69.5	<i>Strontium</i> . . .	Sr	87.6	86.94
Germanium . .	Ge	72.5	71.9	SULPHUR . . .	S	32.06	31.83
Glucinum . . .	Gl	9.1	9.03	Tantalum	Ta	183	181.6
<i>Gold</i> (<i>Aurum</i>)	Au	197.2	195.7	TELLURIUM . .	Te	127.6	126.6
Helium	He	4	4	Terbium	Tb	160	158.8
HYDROGEN . .	H	1.008	1.000	Thallium	Tl	204.1	202.6
Iodine	I	126.85	125.90	Thorium	Th	232.5	230.8
Iridium	Ir	193.0	191.5	Thulium	Tm	171	169.7
<i>Iron</i> (<i>Ferrum</i>)	Fe	55.9	55.5	<i>Tin</i> (<i>Stannum</i>) .	Sn	119.0	118.1
Krypton	Kr	81.8	81.2	Titanium	Ti	48.1	47.7
Lanthanum . .	La	138.9	137.9	Tungsten (<i>Wol-</i>	W	184	182.6
<i>Lead</i>	Pb	206.9	205.35	<i>fram</i>			
Lithium	Li	7.03	6.98	Uranium	U	238.5	236.7
<i>Magnesium</i> . .	Mg	24.36	24.18	Vanadium	V	51.2	50.8
<i>Manganese</i> . .	Mn	55.0	54.6	Xenon	Xe	128	127
<i>Mercury</i> (<i>Hy-</i>	Hg	200.0	198.5	Ytterbium . . .	Yb	173.0	171.7
<i>drargyrum</i>)				Yttrium	Yt	89.0	88.3
Molybdenum .	Mo	96.0	95.3	<i>Zinc</i>	Zn	65.4	64.9
				Zirconium . . .	Zr	90.6	89.9

Names of chief non-metals are printed in capitals.

,, ,, metals ,, ,, italics.

merged in a single liquid substance which possessed quite different properties to those of its components; such a substance is said to be a *chemical compound*. The following experiment will help you to understand the distinction more thoroughly.

EXPERIMENT 38. To study the difference between a mixture of two elements, and a compound of the same two elements. Mix two parts of fine iron filings with one part of flowers of sulphur in a mortar until you can no longer distinguish the sulphur from the iron.

Hold a magnet near the mixture, and observe whether it attracts the iron from the sulphur.

Shake a little of the mixture with water, and notice whether the iron and sulphur separate as they settle.

Agitate a little of the mixture with carbon disulphide, and notice whether it all dissolves or all remains undissolved, as a single substance might be expected to do, or whether the sulphur is dissolved and the iron left.

Examine the powder with a lens, and notice whether it is homogeneous or made up of separate particles of iron and sulphur.

Put some of the mixture into some dilute sulphuric acid, and observe whether the iron dissolves, and gives off hydrogen as it did in Experiment 29, 3.

Mix a little more iron and sulphur, and whilst doing so notice whether they become hot as oxygen and hydrogen do when they combine.

Now take a piece of clean iron-wire gauze rolled into a rod as thick as a cedar pencil, heat it strongly in a blow-pipe flame, and quickly bring it, whilst still hot, into contact with a lump of sulphur held above a basin of water. Observe that when you do this much heat is generated, and that drops of a white-hot substance fall into the water and form metallic masses as they cool. Separate these from the sulphur with which they are mixed, dry them, powder them, and examine them as you examined the mixture of sulphur and iron filings. You will find that you get completely different results from the two sets of experiments. You cannot separate the iron and the sulphur from the metallic masses by mechanical means as before, you cannot extract the sulphur with carbon disulphide, and when you put them in dilute acid they dissolve completely, giving off a gas with a horrible smell, which is combustible like hydrogen, but which produces, when burnt, a strong odour of burning sulphur.

Finally you cannot discern separate particles of iron and sulphur in the new substance even with the most powerful microscope. In short, the sulphur and iron have combined, and the metallic masses consist of a *chemical compound* of iron and sulphur which differs very notably from a mere mixture of its elements such as you had in the first instance*.

43. Combination or synthesis. When we combine hydrogen with oxygen (Expt. 37), or sulphur with iron (42), and again, when we cause magnesium or phosphorus to take oxygen from the air we are dealing with cases of *chemical combination* or *synthesis*. But there are other chemical changes besides combination, and the student should learn to recognize a few of these before proceeding further.

44. Decomposition or analysis. EXPERIMENT 39.

To study the action of heat on oxide of mercury. Heat a little yellow oxide of mercury in a test tube *A* supported by a retort stand, and provided

with a delivery tube *B*. Let the end of *B* dip under a beehive shelf *E* (Fig. 27) placed under water in *C*, and place a cylinder *D*, filled with water, mouth downwards on *E*. Presently bubbles of gas will collect in *D*†, and quicksilver will condense on the cool parts of *A*, until at length all the oxide of mercury will be destroyed.

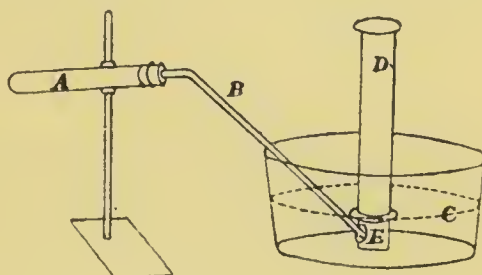


Fig. 27.

A change of this kind is called a *decomposition* or an *analysis*.

Electrolysis. When a compound is decomposed by means of a current of electricity, as in Experiment 36, so that the products appear separately at the two electrodes, the change is called an *electrolysis* (see also 328).

45. Substitution or replacement. EXPERIMENT 40. To study the action of zinc on a dilute acid. Place some granulated

* For a more systematic treatment of this subject see 110 and 122.

† If you plunge a lighted taper or some burning phosphorus into a jar of this gas you will find it supports combustion violently, like oxygen.

zinc in a two-necked bottle *A* (Fig. 28), provided with a thistle funnel *B* and a delivery tube *E*. Cover the zinc with water, and add strong sulphuric acid or strong hydrochloric acid gradually until the liquid appears to boil. Collect several jars, *C*, of the gas given off, marking

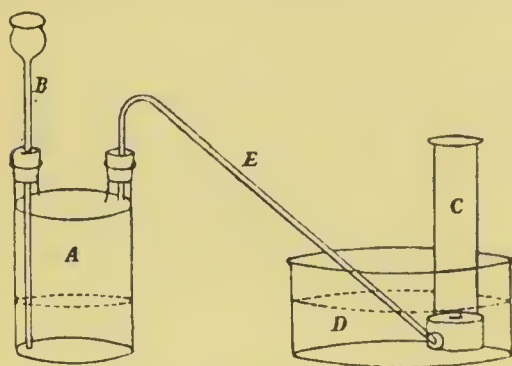


Fig. 28.

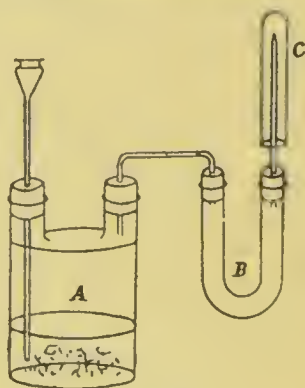


Fig. 29.

them 1, 2, 3, and examine its colour and smell. Then lower a lighted candle into each of the jars in the order in which they were collected. You will find that the contents of the first jar explode almost as violently as the mixed gases obtained from water in Experiment 36,

but that the gas in jar 3 burns quietly with a non-luminous flame like that of hydrogen. If sufficient acid is used all the zinc will be dissolved, though some dark particles, due to impurities, may remain.

Now if the above gas be hydrogen it will produce water, when burnt, by combining with the oxygen of the air (see Expt. 37). Let us therefore burn some of it and try to detect water in its flame.

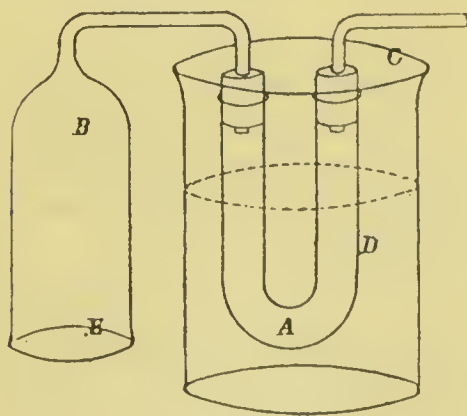


Fig. 30.

EXPERIMENT 41. To endeavour to obtain water by burning the gas from zinc and sulphuric acid. Replace the delivery tube *E* (Fig. 28) by a U tube *B* (Fig. 29) containing calcium chloride, or fragments of pumice-stone moistened with strong sulphuric acid, to dry the gas as it escapes. Collect portions of the dried gas in an inverted test tube *C* (Fig. 29), remove it from the jet and apply a lighted

match to its contents. As soon as the gas burns quietly, ignite it at the jet, bring the flame under the mouth *E* of the tube *B* shown in Fig. 30, and draw the products of its combustion through a U tube *A*, kept cold by water in *D*, by means of a small water-pump or by an aspirator (see Fig. 44, *A*). A colourless liquid will soon collect in the U tube. This freezes at 0° and boils at 100° , and it must therefore be water formed by the union of the hydrogen with the oxygen of the air.

When we consider the results of the above experiment we perceive that whilst hydrogen escaped from the acid, the zinc was dissolved, and that as soon as all the zinc was consumed the generation of the hydrogen came to an end. These phenomena suggest the idea that the zinc expels the hydrogen from the acid and take its place. A change of this kind is called a *substitution* or *replacement*.

The following experiments afford further examples of changes of this kind.

EXPERIMENT 42. To replace quicksilver by copper. Dissolve a globule of quicksilver in two or three drops of nitric acid, dilute the solution with water, and place in it a sheet of copper foil. Examine the solution and the copper from time to time. You will find that the copper soon acquires a coat of quicksilver, and that the liquid becomes green or blue. Remove the copper, dry it with blotting-paper, heat it in a small test tube, and rub the sublimate obtained on the cool parts of the tube with a splinter of wood. It will readily run into visible droplets of quicksilver. From this result it is evident that copper turns quicksilver out of its solution in nitric acid; but does copper take the place of the quicksilver thus removed? To obtain an answer to this question dip the tip of a penknife, or a bit of clean iron wire, in the blue solution. When you do this the iron will become coated with copper, for just as copper replaces quicksilver in a solution so does iron replace copper.

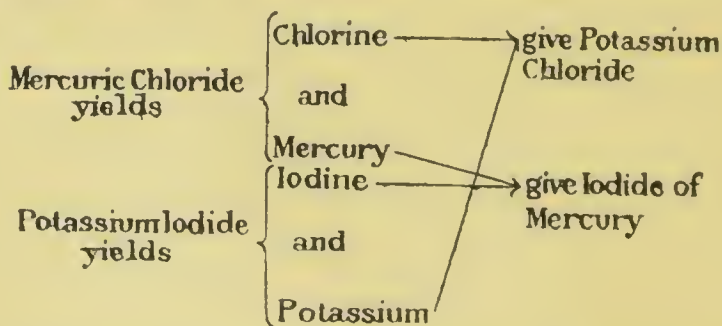
Problems for the Student. 1. Place some fragments of zinc in a weak solution of copper sulphate, observe whether any copper is thrown out of solution, and, if so, whether you can remove all the copper in this way. Can you suggest how to find if any zinc goes into solution?

2. Put a minute fragment of zinc into a drop of solution of nitrate of silver in a watch-glass and observe that *crystals* of silver form. Explain what has happened.

3. Ascertain whether zinc will displace lead from a solution of lead acetate, and, if so, whether any zinc enters into solution to replace the lead.

46. Double decomposition or double exchange. As the composition of substances can be altered by breaking up compounds into simpler substances, by combining simple substances to produce compounds, and by making one substance take the place of another, it may occur to you that chemical changes may also occur in which the constituent parts of two compounds change places. The following experiment affords us an example of a change of this latter kind.

EXPERIMENT 43. Add a solution containing 27 parts of mercuric chloride—this is a compound of the elements mercury and chlorine—to a solution containing 33* parts of potassium iodide. A splendid yellow precipitate, which quickly becomes scarlet, will be formed. Collect this on a filter, saving the filtrate, dry it, and heat a portion of it in an ignition tube. You will find that it melts and boils, giving a sublimate of beautiful yellow crystals which, like iodide of mercury (167), soon become scarlet, especially if they are disturbed. Now we can account for the forming of iodide of mercury from the materials employed, by supposing that the iodine of the iodide of potassium has changed places with the chlorine of the chloride of mercury as suggested in the following diagram :—



If this hypothesis be correct the potassium will remain as chloride in the filtrate from the iodide of mercury. To test the validity of this hypothesis evaporate the filtrate to dryness, heat the residue strongly and try the tests given on pp. 407 and 189 for potassium and chlorine respectively; you will find that both these elements are present in the soluble salt.

A change in which the constituents of two compounds change places, is called a *double decomposition* or a *double exchange*.

* The reason for taking these proportions will appear later.

CHAPTER VI

STUDY OF WATER (CONTINUED)

47. Chemical and physical changes continued (12). When ice is melted, or water turned into steam, and when steam is condensed into water, or frozen into snow, its *composition* remains unaltered. It still retains every particle of the oxygen and hydrogen from which it was formed, and could still be made to yield up those substances by suitable treatment. Such changes as these are called *physical changes*. But when electricity acts on acidulated water, the components of the water are redistributed in new forms as oxygen and hydrogen. A change of this kind, in which a given substance ceases to exist and is replaced by one or more new substances, which differ from the original thing more or less completely in their properties, is a *chemical change*. Thus, when a current of electricity was passed through the wires, plates, and acidulated water in Experiment 36, both the wires, the plates of platinum, and part of the water were altered; but the composition of the wires and plates was not changed at the end of the experiment, the copper and platinum continued to be copper and platinum, for the effect of the current in their case was physical. Its effect on the water was different; some of this ceased to exist, as water, and was replaced by the gases oxygen and hydrogen. The change which this part of the water underwent was a chemical change. Changes of this latter class form the especial subject-matter of chemistry, and the student will do well to try to gain a clear view of the subject by writing answers to the following questions, and submitting them to the criticism of his teacher. Reasons should be given for the answer in each case.

1. When copper sulphate is dissolved in water, is the change a chemical or a physical change?
2. When zinc is dissolved in dilute acid, is the change a chemical or a physical change?
3. When you make a lead tree, is the change which occurs a chemical change?
4. Iron exposed to damp air is converted into iron rust. Is this change chemical or physical?
5. Show that the burning of hydrogen in air is a chemical phenomenon.

6. Are the processes by which your body is nourished by your food chemical or physical changes?

7. Do the processes by which plants are formed from materials found in the air and soil seem to you to be chemical or physical processes?

8. Is the warming of the earth by the sun a chemical or a physical phenomenon?

48. Physical properties of water continued (see section 13 and following sections). We have already learnt that water freezes at 0° (13), that ice melts at the same temperature, and that a definite quantity of heat is absorbed in the latter, and given out in the former change; also that it boils at 100° , absorbing heat (see 15); that even when cold it slowly evaporates, and that its vapour exerts a certain pressure, which may be detected and measured (Expt. 18); and further that water does not contract uniformly when cooled, like other liquids (Expt. 24), and that it expands very considerably on freezing. We have also learnt something about the important part played by many of these properties in nature, but there are a few others which must now be mentioned.

Pure water is destitute of odour and taste, it is transparent, and in small quantities colourless, but when viewed in large masses it is blue, as may be seen from the colour of the ocean and of large masses of ice. On the palate water seems flat and insipid, if quite free from air (taste some freshly distilled water). It is 825 times as heavy as air in the liquid state; but lighter than air in the state of steam.

The weight of one cubic centimetre of water at 4° has been chosen as the unit of weight of the metrical system, and is called a gram, consequently a litre of water (=1000 c.c.) weighs 1000 grams, or a kilogram. We make use of this fact when we want to measure the capacity of flasks or other vessels, as in the following experiment.

EXPERIMENT 44. To find if a 5 c.c. pipette is correct*. Obtain some distilled water, cool it to 4° , by immersing the vessel containing it in melting ice with gentle agitation. Fill the pipette with the cooled water, then empty it, and repeat the operation several times in order to cool the glass, then fill the pipette carefully to the mark, allow the water to flow into a bottle of known weight, close the bottle, and allow it to stand until it is at the temperature of the air, weigh the bottle and its contents. If the pipette be correctly marked it will deliver 5 grams of water.

* This is called 'calibrating' a pipette.

49. The chemical properties of water. Throw a little water on some quicklime (380), and observe the apparently violent action and rise of temperature which ensue. Throw a little burnt phosphorus (257) into some water, and observe that similar signs of activity occur. Let us examine these changes more carefully.

EXPERIMENT 45. To learn what happens when quicklime is slaked. Weigh a lump of freshly made quicklime, place it in a capacious dish, and throw upon it about three-fourths of its weight of water. Observe that it becomes hot, gives off steam, and crumbles to a *dry* powder *. Weigh this powder. You will find it is heavier than the lime from which you made it. Dry it by heating it in a dish on a sand bath, and again weigh it. You will find that part of the increase, at least, is permanent. Evidently the lime and some of the water have *combined*. This experiment illustrates one of the most interesting properties of water, viz. its tendency to combine with compounds such as oxide of calcium and oxide of phosphorus.

Another substance with which water readily combines is sulphuric acid.

EXPERIMENT 46. Place a weighed quantity of strong sulphuric acid in a small basin, in a desiccator (Fig. 21), together with a second basin containing a weighed quantity of water, close the desiccator securely, and put it aside for a few hours or days as may be convenient. Then reweigh both substances. You will find that the weight of the sulphuric acid has increased, and that of the water diminished in a corresponding degree, owing to its absorption by the acid.

EXPERIMENT 47. To find if heat is evolved when water and oil of vitriol are mingled. Place 50 c.c. of oil of vitriol in a beaker containing a thermometer, and add, slowly stirring, about 40 c.c. of water. Observe that the mixture becomes very hot, and that if you plunge a test tube containing a little water in it, the water may be made to boil.

The readiness with which water and oil of vitriol combine is often made useful in chemistry. Thus, in Experiment 41, we dried our hydrogen by passing it over this substance, and the air in a desiccator is kept dry by the same means.

50. Water of crystallization. If you examine the contents of the laboratory store-room you will find that whilst some substances show a tendency to become damp, or to *deliquesce*, in the air, others,

* This powder is *slaked lime*.

such as sulphate of copper, are apt to become dusty, or to *effloresce*, in a manner which suggests that they are drying. We can easily test the truth of this idea by seeing if they lose weight.

EXPERIMENT 48. To find if crystals of copper sulphate and of washing-soda lose weight in dry air. Expose a few grams of *finely* powdered copper sulphate and washing-soda, weighed in dishes, to sulphuric acid in a desiccator and, after a few days, reweigh them. You will find their weight has diminished in each case.

EXPERIMENT 49. To find if water was given off by the crystals used in Experiment 48. (a) Heat 150 grams of washing-soda (soda crystals) in a small retort connected with a well-cooled receiver (Fig. 14). When no more liquid condenses measure or weigh the contents of the receiver, and find the melting-point and boiling-point of the liquid. You will at once recognize that it is water, and from its weight you will conclude that crystals of washing-soda contain nearly two-thirds of their mass of water.

(b) Notice that the residue in the retort is no longer crystalline, and that it becomes hot when a little water is added to it. Dissolve some of it in a little of the water previously warmed and allow the solution to cool. It will again form crystals.

(c*) Make a similar experiment with copper sulphate on a smaller scale. Similar results will be obtained, and you will find that in this case the solid residue is not only devoid of crystalline form, but also is colourless and that both its crystalline form and colour are restored when the water and dried salt are put together again.

Make a similar experiment using common table salt.

The results of these three experiments show us that some salts, though not all, lose water when they are heated, and that the removal of the water is accompanied by the destruction of the crystalline form of the substance. This water is called *water of crystallization*.

The water of crystallization of a substance may usually be expelled somewhat easily, or it may even be given off spontaneously in moderately dry air; in the latter case the substance is said to be *efflorescent*.

Substances containing water of crystallization are often described as *hydrated* to distinguish them from those which contain no water, and which are said to be *anhydrous*. Thus the blue crystals of copper sulphate are 'hydrated,' whilst the colourless sulphate of copper and common salt are 'anhydrous.' Sometimes, as in the case of soda

* If the students work in pairs one member of each pair should do one of the above experiments, and the results should be compared as they proceed.

crystals, the proportion of water of crystallization is very large. Thus, if you purchased 286 tons of soda crystals you would get 106 tons of sodium carbonate and 180 tons of water.

Questions for the Student. 1. How would you test some rectified spirit for water by means of anhydrous copper sulphate?

2. In what case might anhydrous copper sulphate serve for identifying water better than its physical constants?

3. Find the percentage of water of crystallization in (a) copper sulphate, or (b) soda crystals.

Method. Obtain a small porcelain crucible, weigh it, place in it about 2 grams of the powdered crystalline salt and find its weight. Heat the crucible over a Bunsen burner turned low or, better, in an air bath heated to about 120°C . for an hour or so, and when it seems to be dry (how can you judge?) allow it to cool in a desiccator and reweigh it. Repeat this treatment until the salt ceases to lose weight. Then set out your results in such a table as that given below. The results obtained should agree with those given within a few tenths of a per cent.

Weight of crucible and hydrated salt	=	14.49	grams
Weight of crucible only	=	12.42	„
Weight of salt	=	2.07	„
Weight of crucible and anhydrous salt	=	13.89	„
Weight of crucible only	=	12.42	„
Weight of anhydrous salt	=	1.47	„
Weight of hydrated salt taken	=	2.07	„
Weight of anhydrous salt obtained	=	1.47	„
Weight of water expelled	=	0.60	„

Then since 2.07 grams of salt give 0.6 gram of water

$$\begin{aligned}
 &1 \text{ gram of salt will } \frac{0.6}{2.07} \text{ „ „} \\
 &\text{and 100 grams „ „ } \frac{0.6}{2.07} \times 100 \\
 &= 28.9\%
 \end{aligned}$$

Therefore the composition of crystals of copper sulphate is as follows :—

Dry copper sulphate	71.1
Water	28.9
	100.0

Composition of soda crystals:—

Anhydrous salt	.	.	.	.	=	37.1
Water	.	.	.	.	=	62.9
						100.0

51. The nature of solution (32). It is difficult to decide whether solids enter into chemical combination with their solvents when they dissolve, or whether they mingle mechanically with them. If the latter be the truth we should expect a fall of temperature to accompany the dissolving of a solid, since melting is accompanied by absorption of heat (14), and such a fall of temperature does indeed often occur. Thus, for example, if you dissolve some ammonium chloride in water at the ordinary temperature, and at once plunge a thermometer into the solution you will find its temperature is below that of the water.

On the other hand some anhydrous salts, e.g. copper sulphate and soda crystals, readily combine with water, and when these are thrown into water there is a rise of temperature (50). This suggests that combination may occur between the solid and the solvent in these cases, especially as those salts which form coloured hydrates * usually yield solutions of the same colour as their hydrated crystals.

It may be mentioned in conclusion that a connexion has been observed at high temperatures between the fusing-points and solubilities of certain salts, which suggests that, at any rate at high temperatures, solution is a physical phenomenon, and not dependent on the chemical combination of the solid with the solvent. Unfortunately so many salts are altered by the action of very hot water that it has been impossible to follow up these observations (see also 332).

52. Action of water with the metals. Though dampness is well known to promote the rusting of iron, most of the common metals, such as iron, lead, copper, and gold, have but little tendency to interact with water at ordinary temperatures; but early in the present century (1807) Sir Humphry Davy (b. 1778, d. 1829) discovered two metals called *potassium* and *sodium*, which decompose water, and it has long been known that iron is oxidized by steam at a red heat.

EXPERIMENT 50. To study the action of sodium and potassium on cold water. Throw some very small fragments of sodium and

* e.g. Copper sulphate.

potassium separately into small basins containing distilled water. Notice that violent action occurs in each case ; that gas seems to escape, and that both metals *disappear*; that the potassium seems to burn with a lilac-tinted flame, and that the solutions produced have a flavour resembling that of soap; that if red litmus solution be added to the respective solutions they become blue, and that, if they are boiled down in a silver or clean iron basin they yield white solid residues which corrode the skin.

When metals dissolve in acid the gas they set free is hydrogen. Let us see if the gas given off when sodium or potassium dissolves in water is also hydrogen.

EXPERIMENT 51. To examine the gas set free when sodium is dissolved in water. Drop a small fragment of sodium * wrapped in iron-wire gauze into water in a pneumatic trough, and hold above it the open mouth of a cylinder filled with water. When no more gas is evolved close the mouth of the cylinder with a plate of ground glass, remove it from the trough, stand it mouth upwards, remove the glass plate, and quickly bring a lighted taper to the gas. Notice that it burns with a non-luminous flame like that of hydrogen. From this fact, and from its density and other properties it has been proved to be hydrogen.

Sodium then (and potassium) † sets free hydrogen from water. But what becomes of the oxygen? Does it unite with the sodium? Is the white solid produced in the previous experiment oxide of sodium? Unfortunately you cannot conveniently test the truth of this hypothesis experimentally in the case of sodium, but you can do so if you employ iron instead of sodium.

EXPERIMENT 52. To study the action of steam upon red-hot iron. Fill a hard glass tube *B* (Fig. 31), 30 or 40 cm. in length, with clean iron filings, placing plugs of asbestos at *b* and *G'*; attach a delivery tube to *B* at *G* and connect the tube by a well-fitting cork to a flask *D* containing water and some fragments of pipe stem. Heat *B* strongly ‡, taking care not to burn the cork, and when the iron is red-hot boil the water in *D* and allow a lively current of steam to pass over the hot iron, taking care that no water lodges in *B*.

As soon as a few cylinders of gas are collected, remove the delivery

* Do not use potassium for this experiment.

† The experiment cannot be safely made with potassium.

‡ Messrs. Fletcher & Russell of Warrington make inexpensive burners suited for heating glass tubes of various lengths (Fig. 101).

tube from the trough *H*, in order that the water may not be forced back upon the red-hot iron.

The gas which collects in *F* will be found to be colourless, insoluble, very light, and to burn like hydrogen, and as only oxygen or hydrogen is likely to be set free from water [why?] this may be accepted as sufficient evidence that it is hydrogen.

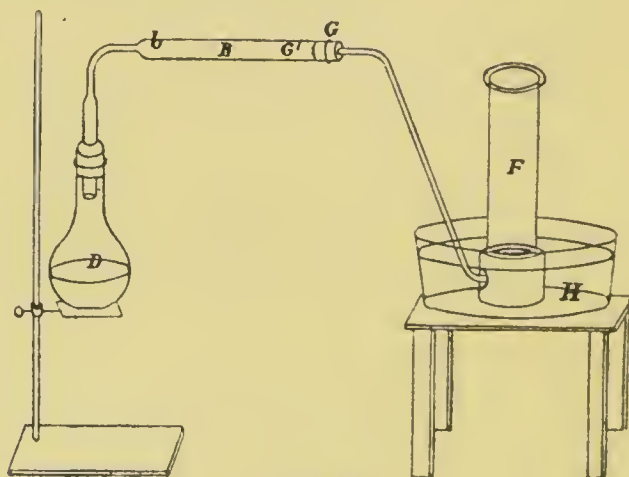


Fig. 31.

EXPERIMENT 53. To ascertain if the residue in *B* (Fig. 31) contains oxygen. Since hydrogen and oxygen form water, we may hope to obtain water from the substance in *B*, if it contain any oxygen, by heating it with hydrogen.

Dry the contents of *B* thoroughly on a water bath, then place them in a tube *E* (Fig. 32), provided with a U tube *D* containing calcium chloride, and an empty U tube *G*. Set up an apparatus for generating hydrogen as previously described, connect it with *D* at *F*, and

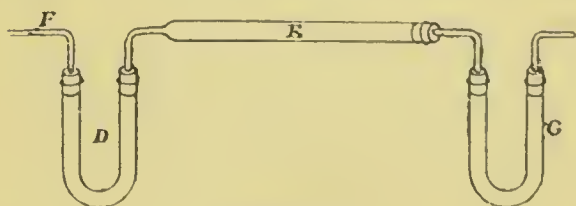


Fig. 32.

after driving all the air from the apparatus, heat *E* to redness whilst passing a current of hydrogen over its contents. Water will condense in *G* if it be kept cool. Now this water must contain oxy-

gen, and this oxygen can only come from the solid produced by the action of iron on steam, for iron is an element. We may therefore conclude that when iron liberates hydrogen from steam, it combines with its oxygen.

53. Oxidation and reduction. In the last two experiments we had examples of 'oxidation' and 'reduction.' In Experiment 52 the iron took up oxygen; this change was an *oxidation*. In Experiment 53 the iron oxide lost its oxygen, becoming *reduced*, as we say, to iron again. Such a change as this latter one is called a *reduction*. This subject will be more fully discussed in 132.

THE COMPOSITION OF WATER AND THE LAWS OF CONSTANT AND MULTIPLE PROPORTIONS.

54. Cavendish's experiments. From the results of Experiments 36, 37, and 41, we have learnt that water is composed of hydrogen and oxygen in the proportions of two volumes of hydrogen to one of oxygen.

Cavendish (b. 1731, d. 1810) was the first to make exact experiments on the composition of water (1781). He discovered that when hydrogen is exploded with oxygen, water is the sole product, and that the two gases combine very nearly in the proportions given above. Since his time the composition of water has been the subject of numerous researches, which fall readily into two classes:—

1. Those in which the volumes of the combining gases are determined.
2. Those in which their weights are measured (55).

Finding the composition of water by volume. When oxygen and hydrogen are set free from water by electricity, the volume of the oxygen is found to be rather less than half that of the hydrogen. This is due partly to the unequal solubilities of the two gases in water, partly to the production of another oxide of hydrogen, and partly to the circumstance that some of the oxygen is liberated in a peculiar and condensed form called ozone (124). Consequently it is difficult to find the exact composition of water by the electrolytic method (Expt. 36).

EXPERIMENT 54. To find the proportions by volume in which hydrogen and oxygen form water. Obtain a Hofmann's eudiometer (Fig. 33) fixed on a stand, fill the arm *A* with mercury, and incline the eudiometer so as to transfer the mercury to *E*. Prepare some oxygen from chlorate of potassium (117), and when the apparatus is free from air, place the end of



Fig. 33.

the delivery tube under the mercury at *A*, inclining the tube a little in the direction of the arrow *G*, and collect a few cubic centimetres of oxygen in *E*.

Now pour mercury into *A* till it stands at the same level in *A* and *E*, so that the gas may be measured at the pressure of the atmosphere*.

Read the position of the mercury in *E* by means of a scale placed behind it, or mark its position by a strip of gummed paper. Let us call this *I*.

When you measure the gas, expose the eudiometer to the warmth of your body as little as possible, and do not work near a stove or furnace, because gases expand considerably when they are heated†. If you tie a thermometer to *E*, you will be able to assure yourself that all your measurements are made at about the same temperature.

Set up an apparatus for making dry hydrogen (Expt. 41) provided with a very long thistle funnel, and a flexible delivery tube. Add some hydrogen to the oxygen in *E*, after first reducing the level of the quicksilver, and measure the volume, *II*, of the mixture of oxygen and hydrogen at the atmospheric pressure as before.

Fill *A* with mercury to *G*, close its mouth firmly with the thumb, and pass an electric spark between *E E* to explode the gases. Remove the thumb from *A*—a great contraction will occur when you do this—adjust the pressure as before, find the volume, *III*, of the residue, and ascertain whether it consist of oxygen or hydrogen by filling *A* with mercury, transferring the gas to *A*, and testing it with a lighted match.

If *E* were of uniform bore throughout its length, the relative volumes of oxygen, of oxygen and hydrogen, and of the residue, might be deduced from the length of tube occupied by each, but as *E* is probably not uniform‡, you must fill the spaces *I*, *II*, and *III* with mercury, and either measure the mercury required in a measuring-glass, or weigh it and calculate its volume from the fact that 1 c.c. of mercury weighs 13.59 grams.

Let us suppose that 10.5 c.c. of oxygen were taken, that 30 c.c. of hydrogen were added, and that a residue of 8.9 c.c. of hydrogen remained.

* See 63.

† Try the effect of blowing a little warm water over *E* from a wash-bottle.

‡ A graduated eudiometer like that shown in Fig. 66 may also be used.

Then, since $30 - 8.9 = 21.1$, it follows that 21.1 c.c. of hydrogen have combined with 10.5 c.c. of oxygen. But

$$10.5 : 21.1 :: 1 : 2 \text{ (nearly).}$$

Therefore one volume of oxygen combines with two of hydrogen.

Sources of error. The above experiment would not give very accurate results for various reasons:—

(i) Owing to the curvature of the surface of mercury, we cannot measure a gas quite correctly over this liquid unless we correct for the error thus caused.

(ii) It is very difficult to read the true level of the mercury with the eye.

(iii) It is difficult to maintain the gas at a uniform temperature unless we surround *E* with a vessel of water at some fixed temperature.

(iv) The method of adjusting the pressure of the gas is not very satisfactory. For a more exact method see Experiment 17.

(v) The residue left in *E* after exploding the mixture was not pure oxygen, nor pure hydrogen, for water vapour was also present, and this should have been allowed for when *III* was measured.

The volumes of gas measured were small, and hence the effects of the various errors would be relatively large. These errors might, it is true, tell in opposite directions and thus tend to neutralize one another, yet, in a given case, all or most of them might act in the same direction and then their collective effect would be very great.

In spite of the above-mentioned difficulties various attempts have been made to re-determine the composition of water by volumetric methods. A set of experiments, made by Dr. Scott, who employed large volumes of the two gases, shows that 2.0024 volumes of hydrogen combine with 1 volume of oxygen. Another, by Mr. Morley, gives the ratio of the volume of the hydrogen to that of the oxygen as 2.0027 to 1.

Exercises for the Student. (Answers will be found on p. 513.)

1. If you mix 225 c.c. of oxygen with 120 c.c. of hydrogen and explode, what gas and how much of it will be left?

2. If you explode 150 c.c. of air with 100 c.c. of hydrogen, how much nitrogen and hydrogen respectively will be left?

3. When 100 c.c. of air and 100 c.c. of hydrogen were mixed and exploded 137 c.c. of gas were left. Calculate the proportion of oxygen in this air.

4. How much air would you require to exactly convert 1114 c.c. of hydrogen into water, and how much nitrogen would be left?

5. 16.7 c.c. of air when mixed with hydrogen to 29 c.c. and exploded left 18.5 c.c. Find the composition of the original air.

EXPERIMENT 55. To measure the steam produced when oxygen and hydrogen combine. Surround the closed end *A* of a Hofmann's eudiometer with a glass jacket *B* (Fig. 34), held in position by corks and a clamp *G*, and provided with two small tubes *D* and *E*. Fill *A*

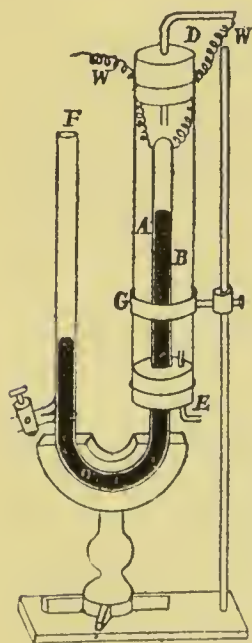


Fig. 34.

with mercury and introduce a few cubic centimetres of the mixed gases produced by electrolysing water, after drying them. Connect *D* with a vessel containing boiling aniline and *E* with a condenser, and when *B* is filled with aniline vapour adjust the pressure on the gases in *A* and note their volume. Then explode the gases taking the usual precautions, adjust the pressure on the resultant steam as before and read its volume. You will find that three volumes of oxygen and hydrogen yield *only* two volumes of steam.

This striking fact must never be forgotten, for beginners are apt to assume that the volumes occupied by gases are as unalterable as their masses, which is not the case.

55. The composition of water by weight. **EXPERIMENT 56. To find the composition of water by reducing oxide of**

copper with hydrogen and weighing the products. (Fig. 35.) Place some granular copper oxide in a bulb *A* of hard glass, provided with narrow tubes *D E*, warm the apparatus and draw dry air through it, then close its ends with caps made of india-rubber tubes plugged at one end with glass rods, and when it is cool weigh it. Fill a tube *B* with pumice-stone moistened with sulphuric acid, close its ends, weigh it and join it to *A*. Set up an apparatus for generating dry hydrogen and connect it to the end *E* of *A*. Pass hydrogen through *A* and *B* till all the air is expelled. Then heat *A* to dull redness and pass a *slow* stream of hydrogen over the oxide. Water will be formed, part will condense at *C*, the rest will be absorbed by the acid at *B*, and at the same time the oxide of copper will

be reduced to metallic copper. When about a gram of water has condensed in *C* cease to heat *A*, but continue to pass hydrogen through the apparatus for some time in order to sweep all the water from *A*. Then separate *A* from *B*, close their ends as before, and when they are cool reweigh them.

Independent experiments have shown that oxide of copper does not lose oxygen at a low red heat, therefore if you have neither admitted oxygen into the apparatus nor allowed any water to escape, all the oxygen lost by the copper oxide must now exist as water, in *B*. Therefore if you deduct the weight of the oxygen lost by *A* from that of the water gained by *B* you will find the hydrogen in this water. Enter your results in such a form as the following:—

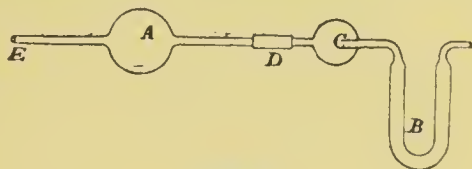


Fig. 35.

<i>A.</i>	Weight of <i>A</i> before reducing the oxide	=	40.4 grams
	„ „ after reducing the oxide	=	32.4
	Weight of oxygen	=	8.0
<i>B.</i>	Weight of <i>B</i> and water	=	60.0
	„ of <i>B</i> alone	=	51.0
	Weight of water formed	=	9.0
<i>C.</i>	Weight of water found in <i>B</i>	=	9.0
	„ „ oxygen lost by <i>A</i>	=	8.0
	Weight of hydrogen	=	1.0

Let us suppose that 9 grams of water were found in *B* and that 8 grams of oxygen were lost by *A*. Then, since nothing can be created or destroyed in a chemical change, 1 part of hydrogen must have united with 8 parts of oxygen to form 9 parts of water. Expressed as a percentage this shows that water contains

Oxygen	88.88
Hydrogen	11.11
	99.99

The results obtained by the student should be moderately near to those given above.

56. Determination of the composition of water by

Dumas and others. The composition of water by weight has been carefully determined by a number of observers who employed processes analogous in their main features to that just performed. It would be impossible to describe all their experiments, but the following account of a remarkable series made by Dumas in 1842 will give some idea of the pains and skill which have been spent upon this work.

Dumas commenced fifty experiments like that described below and succeeded in completing nineteen. The whole series occupied about a year, and he has told us, that although his experiments were begun at an early hour, and though very complete preparations were made beforehand, it often happened that the sun rose on the succeeding day before they were completed.

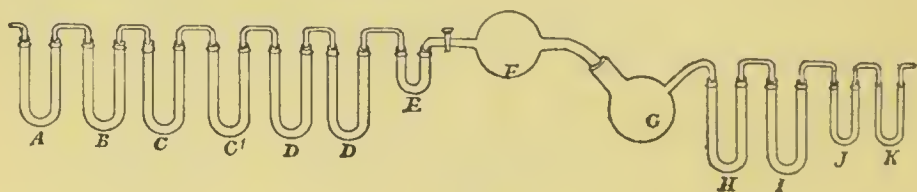


Fig. 36.

In Dumas' experiments hydrogen, generated from zinc and dilute sulphuric acid in a bottle to which air could not gain admittance, was passed through the tubes marked *A B C D* to purify it*. *A* contained pumice-stone moistened with solution of lead nitrate to remove hydrogen sulphide, which may be present in hydrogen made from zinc; *B* contained solution of a silver salt to remove arsenetted hydrogen; *C* and *C'* contained potash to remove acid impurities, and help to dry the gas, part of the potash in *C* was in solution, the rest in the solid state, and all the potash in *C'* was solid; *DD* contained phosphoric oxide kept cool to remove the last traces of water. *E* was used to test the purity of the gas; it contained phosphoric oxide and was weighed before and after each experiment. If the mass of *E* remained unaltered, it was known that dry hydrogen had passed into *F*, for any moisture which might escape *DD* would be absorbed to a greater or less extent in *E*, and so add to its weight. Oxide of copper, made quite dry by heating it strongly, was placed in a bulb *F*; this bulb was made of glass which would bear a high temperature for many hours without softening or breaking and without undergoing the least change in weight. The hydrogen on reaching *F* reduced the

* Hydrogen prepared from magnesium might now be used for this experiment. It would only be necessary to treat the gas thus prepared with alkali and to dry it.

copper oxide, forming water and metallic copper; most of the water condensed in *G*, the rest was absorbed by solid potash in *H* and the last traces by phosphoric oxide in *I*. *J* contained phosphoric oxide and was employed to make sure that no water escaped from *I*; *K* also contained phosphoric oxide and served to prevent moisture from the outer air reaching *J*. The bulb *F*, with its contents, was weighed when cold and full of air before and after the experiment, and the decrease in its weight gave the weight of the oxygen removed by the hydrogen.

G, *H* and *I* were also weighed before and after making the experiment. If *m* represents the mass of water collected in *G*, *H* and *I*, and if *n* represents the oxygen lost by the copper oxide, then *m* - *n* gives the weight of hydrogen combined with *n* of oxygen to form *m* of water.

From the results of nineteen successful experiments Dumas found the percentage composition of water to be:—

Oxygen	88.864
Hydrogen	11.136
	100.000

Several chemists have employed some modification of the above process for finding the composition of water; others, like Dr. Scott, have measured the volumes in which the two gases combine, and then, aided by the very exact determinations of their densities made by Regnault, and more recently by Lord Rayleigh, have calculated the weights of these volumes. The following table gives some of the chief results obtained. For the sake of simplicity the amount of oxygen which was found to combine with unit mass of hydrogen in each case is given.

COMPOSITION OF WATER.

I.	II.
<i>Name of Experimenter.</i>	<i>Weight of oxygen found to combine with unit mass of hydrogen.</i>
1. Dumas	7.98
2. Erdmann and Marchand	7.98
3.* Cooke and Richards	7.934
4.† Keiser	7.974
5. Scott	7.931
6. Morley	7.939

Gravimetric
methods.
Volumetric
methods.

* The hydrogen was weighed in large flasks.

† The hydrogen was weighed when occluded in palladium

57. The law of constant proportions. The results of a great number of researches have led chemists to conclude that a *given compound is always formed by the union of the same elements in the same proportions*. This is known as the 'Law of Constant Proportions.' The evidence upon which it rests consists in the whole body of chemical facts at present ascertained. The nature of this evidence is well illustrated by the above table which shows that a number of chemists, employing different methods and using quite separate supplies of material, have come to almost exactly the same conclusion concerning the composition of water. Our confidence in the law is based, first on the existence of a great number of well established facts which support it, and secondly on the absence of any well established fact which is inconsistent with its truth.

58. A second compound of oxygen and hydrogen. Hydrogen peroxide. Although a given compound always contains the same elements in the same proportions, it by no means follows that these elements only unite in one fixed ratio. Thus 7.93 parts of oxygen unite with 1 part of hydrogen to form water, but oxygen and hydrogen also unite in other proportions to form a second compound called *peroxide of hydrogen*.

EXPERIMENT 57. **To make hydrogen peroxide.** Dissolve 3 or 4 grams of finely powdered barium peroxide, gradually, in 10 c.c. of strong hydrochloric acid diluted to 30 c.c. with water, and well cooled. Filter the solution, and add a little of it to some very dilute solution of permanganate of potassium. Notice the change of colour and effervescence that occur. On testing the gas evolved you will find it to be oxygen.

Shake another portion of the solution with some solution of potassium bichromate, and some ether. On standing, the ether will quickly rise above the water, and exhibit a fine blue colour.

Warm a few drops of the solution with dilute solution of indigo, and note its bleaching power.

Expose a strip of filter-paper, previously soaked in dilute solution of acetate of lead, to hydrogen sulphide, then dip the blackened paper in the above solution. The black sulphide of lead will gradually change into lead sulphate which is colourless. From these tests, it is evident that the solution prepared as above described contains something other than water, something we have not met with before. This new substance is *peroxide of hydrogen*.

EXPERIMENT 58. To discover the nature of peroxide of hydrogen. (Use the purchased material.)

(a) Cool some solution of hydrogen peroxide in a test tube by means of a freezing mixture of ice and salt, and find if it freezes at 0° , or at a lower temperature.

(b) Find the weight of 1 c.c. of the liquid. If it weighs much more or less than a gram, making due allowance for errors of experiment, it cannot be water. [Why not?]

(c) Fill four-fifths of *A* (Fig. 37) with quicksilver and the remainder with solution of peroxide of hydrogen, invert it in a basin of quicksilver, and warm the peroxide carefully with a Bunsen flame. Notice that a gas is liberated. Then close the open end of *A* with the thumb, remove the tube from the basin, and test its contents. You will find that the gas is tasteless, odourless, practically insoluble, and ignites glowing carbon.

(d) Heat some granulated silver in a flask with some solution of hydrogen peroxide, and place a thermometer in the liquid. Notice that it begins to effervesce at about 80° or 90° * giving off oxygen, and that its temperature gradually rises to 100° . If you take the freezing-point of the residue you will find it to be 0° . Therefore you may conclude that the peroxide can be resolved into oxygen and water, for the silver remains unaltered at the end of the experiment. (See Catalysis, 117.)

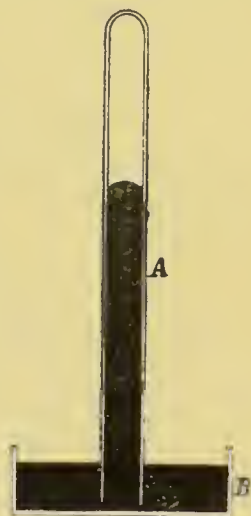


Fig. 37.

The results of the above experiments, and especially those of *c* and *d* strongly point to the conclusion that hydrogen peroxide is a new compound of hydrogen and oxygen which contains more oxygen than water. In its most condensed state, for it has not been obtained free from water, it forms a syrupy liquid, with a harsh taste, which corrodes the skin, and decomposes explosively at 100° . From certain analogies between this substance and certain other oxides, it is believed that the pure compound would contain 5.9% of hydrogen and 94.1% of oxygen, and if we compare its composition with that of water we get the following :—

* The exact temperature depends on the strength of the solution.

I. <i>Composition of Water.</i>		II. <i>Composition of Hydrogen Peroxide.</i>	
Hydrogen	11.11	Hydrogen	5.9
Oxygen	88.88	Oxygen	94.1
	<u>99.99</u>		<u>100.0</u>

A comparison of these figures does not throw much light upon the relative composition of the two substances. But if we calculate how much oxygen is united with 1 part of hydrogen in each compound we find that the proportion of oxygen in the peroxide is very nearly twice as great as in water:—

I. <i>Composition of Water.</i>		II. <i>Composition of Hydrogen Peroxide.</i>	
Hydrogen	1	Hydrogen	1
Oxygen	7.93	Oxygen	16
But 7.93 : 16 :: 1 : 2 (nearly).			

59. The law of multiple proportions. Water and hydrogen peroxide illustrate in a very simple manner a third and very important law of combination known as the law of multiple proportions: viz.: *That when two elements form more than one compound the quantities of one element which combine with a fixed quantity of the other exhibit a simple multiple relation.* (Continued in 80.)

Problem for senior students. Ethane contains 80 % of carbon with 20 % of hydrogen: methane contains 75 % of carbon to 25 % of hydrogen. Show that these compounds illustrate the law of multiples.

CHAPTER VII

THE ATMOSPHERE AND COMBUSTION

60. That atmospheric air has weight. We have learnt, from the results of several experiments, that when atmospheric oxygen is absorbed in burning the weight of the thing burnt is always increased. Therefore, since nothing can be created or destroyed in

chemical changes (5), we must conclude that air, like the solid and liquid forms of matter, is influenced by gravity or, as we say, has weight. We can verify this by the following simple experiment.

EXPERIMENT 59. To find the weight of a litre of atmospheric air. Attach a glass tube *C* carrying a piece of india-rubber tube *D*, and a screw clamp *S*, to a flask *A* by means of an india-rubber cork *B*, selecting for the purpose the largest flask your balance will conveniently carry*. Suspend the flask from one of the arms of a balance, and counterpoise it by placing weights or, better, a similar flask on the opposite pan. Exhaust *A* as completely as you can by means of an air-pump†, close *S* securely, reweigh the flask, and write down your results as suggested below.

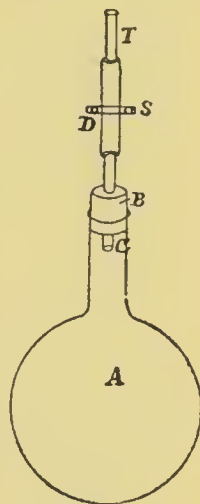


Fig. 38.

Weight of flask and 250 c.c. of air	=	150.52 grams
„ „ only	=	150.20
„ 250 c.c. of air	=	0.32
∴ The weight of 1 litre of air is $\frac{0.32 \times 1000}{250} = 1.28$ grams.		

The true weight of a litre of air is nearly 1.29 grams, but the value found is likely to be higher or lower than this, partly because large globes offer a good deal of surface to the air, and are very greatly affected by draughts, and a student cannot usually secure a working-place quite free from draughts; and partly for other reasons which will be considered in 63 and 64.

61. Nitrogen. Nitrogen is the gas which Lavoisier obtained as a residue (see 4) after absorbing the oxygen from atmospheric air by means of heated quicksilver. It can be more conveniently prepared from air by absorbing the oxygen with copper.

EXPERIMENT 60. To prepare nitrogen from atmospheric air. Fill a gas-holder (Fig. 39) with water to the level *l*l, from its reservoir *R*. Connect the tube *E* to a hard glass tube, such as was used in Experiment 52, filled with copper turnings heated to redness.

* Read the notes at the end of this section before making the experiment.

† The Geryk pump is inexpensive and suitable for work of this kind.

Open T and T^2 that water may flow into B and drive a slow current of air over the copper, and then into cylinders placed to receive it

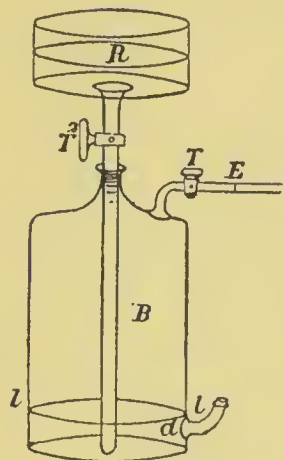


Fig. 33.

as in previous similar experiments. When you have collected a few cylinders of the gas, note its want of taste, smell and colour, and its apparent insolubility in water. Then plunge a burning candle fixed on a wire, and also ignited sulphur and phosphorus held in deflagrating spoons (A , Fig. 40) into jars of the gas, and notice that all are extinguished by the nitrogen. Notice also that the copper becomes black owing to its conversion into oxide of cop-

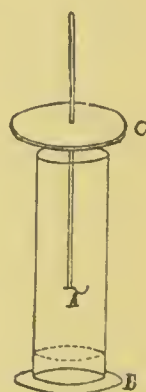


Fig. 40.

per. How could you test the truth of this statement experimentally? (see Expt. 53).

62. The analysis of air. Phosphorus was at one time employed to absorb oxygen in the analysis of air, but as it does not take up all the oxygen from a mixture such as air its use has been abandoned.

EXPERIMENT 61. Eudiometric analysis of air*. The following process is based on the fact that if two volumes of hydrogen are exploded with one of oxygen both gases disappear and are replaced by a minute drop of water (see 54).

Introduce about twenty cubic centimetres of dry air into the eudiometer (Fig. 33), find its volume at atmospheric pressure, add about half as much dry hydrogen, remeasure the mixture, and explode it by an electric spark. To remove the water-vapour formed, fill A with mercury to G , then fill up with oil of vitriol, close the mouth of A with a rubber cork and incline the eudiometer so as to transfer a few drops of the oil of vitriol to E . As soon as the volume of the residue in E becomes constant, remeasure it.

Let us suppose that the following results were obtained:—

Volume of air taken		20.2 c.c.
Volume of air and hydrogen		33.0 c.c.
Volume after exploding the mixture		21.0 c.c.

* This is also known as the 'Cavendish method.'

From these figures we see that $33 - 21 = 12$ c.c. of oxygen and hydrogen have combined.

Two-thirds of this, or 8 c.c., was hydrogen, and one-third, or 4 c.c., oxygen (see Expt. 54). Therefore, as we added 12.8 c.c. of hydrogen to the air and only used up 8 c.c., we may conclude that all the oxygen was burnt, and that only 4 c.c. of it were present in the air taken.

Cavendish first determined the composition of air by the above method. He found that 100 volumes of air contain about 21 volumes of oxygen.

EXPERIMENT 62. To find the volume of oxygen in air by absorbing it with pyrogallol and potash. The apparatus referred to below consists of two parts—viz. of a modification of the Hofmann eudiometer Fig. 41, I, and of a gas pipette or absorption tube II. The former, if provided with wires, may be used in place of the Hof-

mann eudiometer. The apparatus is not costly and can be manipulated easily by the older students.

Dissolve 5 grams of pyrogallol in 15 c.c. of water, add it to 120 grams of caustic potash dissolved in 80 c.c. of water, and draw the solution into the pipette, through *A*, in such quantity that when *B* is filled *C* is almost empty. Close *A* and *E*, to prevent access of air to the solution. Pour water into the reservoir *R*, open taps *T* and *T*² and raise *R* till *G* is filled with water. Then lower *R* and admit some air to *G*. Close *T* and, leaving *T*² open, measure the air taken at atmospheric pressure (Expt. 54), and note the temperature and the height of the barometer.

Connect *A* to *H* by the tube *K* of narrow bore after filling *B* and

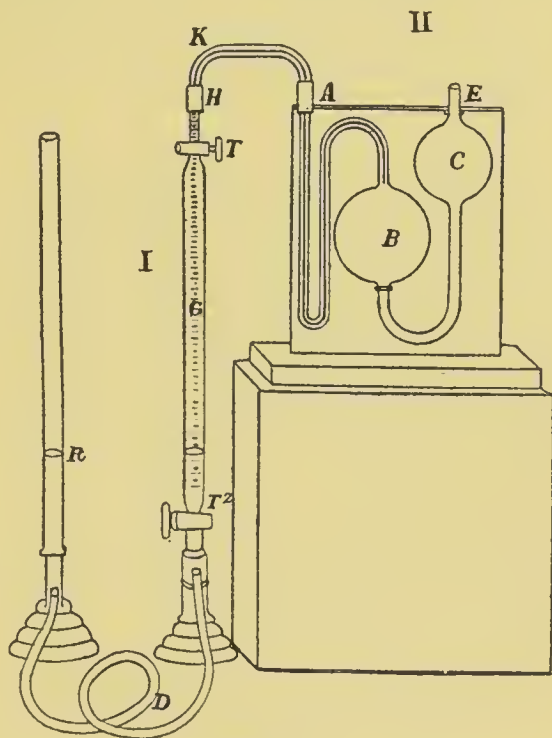


Fig. 41.

A with the absorbent solution. Open T and T^2 , raise R and force the air from G into B . Close T , disconnect the pipette from the eudiometer, and shake the air with the absorbent vigorously for some minutes. Then transfer the residual air to G and remeasure it, noting, as before, the temperature and the height of the barometer at the time of measurement.

Two measurements should be made and the results obtained should not differ greatly. The same absorption apparatus $B\ C$ may be filled with other reagents and used in the analysis of other gaseous mixtures.

63. To correct the volume of a gas for the effects of atmospheric pressure—Boyle's Law. In making Experiment 54 we learnt, incidentally, that the volume occupied by a given mass of a gas may be altered considerably by varying the pressure upon it. It would be convenient if we could always measure gases at a standard pressure, but unfortunately atmospheric pressures are so inconstant that this cannot be done, and therefore we have to introduce a correction based on a law discovered by Robert Boyle and known as 'Boyle's Law.'

EXPERIMENT 63. To study the influence of pressure on the volume occupied by a fixed mass of a gas. Dry the eudiometer used in the last experiment, and bind the india-rubber tube D with canvas to strengthen it.

Pour quicksilver into R , allowing it to rise in G till the latter contains 10 c.c. of air at atmospheric pressure, then close T . Raise R till the air in G measures 5 c.c., and measure the difference between the level of the mercury in R and in G . You will find it to be equal to the height of the barometer. Therefore to reduce the volume of the air by one half it was necessary to double the pressure.

Next lower R until the volume of the air becomes 20 c.c. and again measure the distance between the level of the quicksilver in R and in G . You will find that in order to increase the volume of the air from 10 c.c. to 20 c.c. it has been necessary to reduce the pressure by one half. If you repeat the experiment using other gases, such as oxygen and hydrogen, you will obtain similar results.

These facts are expressed briefly by 'Boyle's Law' which states that—*The volume occupied by a given mass of any gas is inversely proportional to its pressure if its temperature be constant.*

Thus if V and V' are the volumes occupied by a given mass of a gas at the pressures P and P'

$$\frac{V}{V'} = \frac{P'}{P}$$

or

$$VP = V'P'$$

Let us suppose that 41 c.c. of air were taken in Experiment 62, and that the barometer stood at 740 mm. Then to find the corresponding volume at 760 mm. we make the following calculation in which V' stands for the required volume at 760 mm. whilst 41 is the observed volume at 740 mm.

$$\begin{aligned} V' \times 760 &= 41 \times 740 \\ \therefore V' &= 41 \times \frac{740}{760} \\ &= 39.9 \text{ c.c.} \end{aligned}$$

64. To correct the observed volume of a given mass of a gas for the effects of temperature—Charles' Law. (This law was also discovered by Dalton.)

EXPERIMENT 64. To compare the volume of a given mass of a gas at 0° with its volume at 100° *. Clean and dry the flask used for Experiment 59 (Fig. 38), and fix its cork very securely. Immerse the flask, with the clip open, in a vessel of boiling water for a few minutes, then close the clip taking care that the water boils freely when you do so. Allow the flask to cool, then immerse it completely in ice and water and open the clip. When water ceases to enter the flask, remove the latter from the cold water, take out the cork, measure the water in the flask, and find also how much water the flask will hold when the cork is in position.

Let us suppose that the flask holds 300 c.c. of water when full, and that 80 c.c. of water entered when the flask full of air at 100° was cooled to 0° .

Then it follows that an amount of air which occupies 300 c.c. at 100° only occupies 220 c.c. at 0° .

Since 220 c.c. of air at 0° expand by 80 c.c. in rising through 100°

$$\begin{array}{ccccccc} \therefore 1 \text{ c.c.} & & & & \frac{80}{220} & & 100^\circ \\ \text{and } 1 \text{ c.c.} & & & & \frac{80}{220 \times 100} & & 1^\circ \dagger \end{array}$$

And $\frac{80}{220 \times 100} = \frac{1}{275}$

* This is a modification of an experiment first described by Prof. Ramsay.

† Assuming it expands regularly; as experiment shows.

That is to say, one cubic centimetre of air heated from 0° to 1° is increased by $\frac{1}{273}$ of a cubic centimetre.

This quantity, $\frac{1}{273}$ *, is called the *coefficient of expansion of air*, and if we were to determine the coefficients of expansion of several other gases, for example of oxygen, hydrogen, and nitrogen, we should find them to have very nearly the same value as air, for all permanent gases expand and contract uniformly and at the same, or nearly the same rate, when they are submitted to changes of temperature.

The law of Charles was first properly verified by Gay-Lussac, who adopted a higher value for the coefficient of expansion than that now accepted. It should be added that the more exact experiments made by his successors show us that the law is only approximately true.

65. The absolute scale of temperature—Absolute Zero.

One cubic centimetre of a permanent gas at 0° expands to the amount of $\frac{1}{273}$ of a cubic centimetre for every rise of 1° , or in other words 273 c.c. at 0° become 274 at 1° , 275 at 2° , and so on. On the other hand, 273 c.c. of a gas at 0° would become 272 at -1° ; 271 at -2° ; 270 at -3° ; 170 at -103° , and 0 at -273° .

Of course no one has actually traced the rate of contraction of any gas to -273° , and in fact all gases become liquid before they reach so low a temperature; but since they behave, at ordinary temperatures, as if they would vanish, or, at least, would occupy insensible volumes at -273° , this temperature affords us a very convenient reference point in thermometry, which is known as the *Absolute Zero*, and which forms the starting-point of a scale of temperatures called the 'Absolute Scale.'

Degrees on the absolute scale corresponding to temperatures on the centigrade scale are easily calculated by adding 273 to the latter. Thus :—

I.	II.	III.
$-273^{\circ} \text{ C.} + 273$	gives	$0^{\circ} \text{ Absolute.}$
$-272^{\circ} \text{ C.} + 273$	„	1° „
$-271^{\circ} \text{ C.} + 273$	„	2° „
$-1^{\circ} \text{ C.} + 273$	„	272° „
$0^{\circ} \text{ C.} + 273$	„	273° „
$+1^{\circ} \text{ C.} + 273$	„	274° „
$+2^{\circ} \text{ C.} + 273$	„	275° „
$+273^{\circ} \text{ C.} + 273$	„	546° „

* The true value is approximately $\frac{1}{273}$.

In the table which follows, temperatures from -273° C. to $+273^{\circ}$ C. are given in column I; the corresponding temperatures on the Absolute Scale in II, and the relative volumes of a mass m of a gas at constant pressure in III. This table expresses the fact that *the volume occupied by a given mass of a true gas* is directly proportional to its Absolute Temperature when its pressure is constant.*

I. Temperatures on Centigrade Scale.	II. Temperatures on Absolute Scale.	III. Volumes of the Mass m of a gas.
-273°	0°	0
-272°	1°	1
-1°	272°	272
0°	273°	273
$+1^{\circ}$	274°	274
$+2^{\circ}$	275°	275
$+273^{\circ}$	546°	546

Now let us apply the above considerations to the analysis of atmospheric air upon which we were lately engaged, remembering that it is usual to take 0° C. as the standard temperature in all such work.

The volume of the air taken was found to be 39.9 c.c. (p. 75) at 760 mm. Let us suppose that it was measured at 27.3° .

According to Charles' Law, as stated above, if V be the volume of a given mass of a gas at any temperature on the absolute scale T , and V' its volume at another temperature T' , then

$$V \times T' = V' \times T.$$

Now in the case before us $V = 39.9$ c.c., $T = 273 + 27.3$, and $T' = 273 + 0$, whilst V' is the quantity to be found. From the above we see that

$$V' = \frac{V \times T'}{T}.$$

Therefore

$$\begin{aligned} V' &= \frac{39.9 \times 273}{273 + 27.3}; \\ &= \frac{39.9 \times 10}{11} \\ &= 36.3 \text{ c.c.} \end{aligned}$$

* A true gas may conveniently be defined as one which obeys the laws of Charles and Boyle.

Therefore 36.3 c.c. of air were taken for analysis at 0° and 760 mm. Let us further suppose that the residue of nitrogen measured 28.7 c.c. at 912 mm. and 54.6° C.

1. To find its volume at 760° mm. we have—

$$28.7 \times \frac{912}{760}.$$

2. To find its volume at 0° we have—

$$28.7 \times \frac{273}{273 + 54.6}.$$

Combining these two we get—

$$28.7 \times \frac{912}{760} \times \frac{273}{273 + 54.6} = 28.7 \text{ c.c.}$$

By deducting this from the volume of the air we find that 36.3 c.c. of air contain 7.6 c.c. of oxygen.

But if 36.3 c.c. of air contain 7.6 c.c. of oxygen,

$$100 \quad \text{,,} \quad \text{will} \quad \text{,,} \quad 7.6 \times \frac{100}{36.3} = 20.9.$$

Therefore we have for the composition of air:—

Nitrogen	79.1
Oxygen	20.9
	100.0

The student should work out the following numerical exercises before proceeding to what follows.

Exercises. (Answers will be found on p. 513.)

1. 250 c.c. of hydrogen are heated from 0° to 39° . Find the new volume.
2. 750 c.c. of a gas are heated from -39° to 52° . Find the new volume.
3. The pressure on 12 c.c. of a gas is 7 atmospheres; it is then reduced to 847 mm. Find the new volume.
4. 271 c.c. of oxygen at 269° and 900 mm. are cooled to -51° at 666 mm. Find the new volume.
5. What will 76.7 litres of air at 14° and 740 measure at 0° and 760?
6. At what temperature will air have the same density as hydrogen at 0° ?
7. What will 1000 c.c. of air at normal temperature and pressure become at 16.5° and 1470 mm.?
8. What will 672 c.c. of nitrogen at -49° and 1111 mm. measure at 357° and 1890 mm.?
9. At what temperature will a litre of air weigh a gram? (At 0° 1 litre of air weighs 1.293 grams.)

66. A method of finding the composition of air by weight.

An exact method of finding the proportions of oxygen and nitrogen in the air is that of Dumas and Boussingault.

A large globe *A* was exhausted as completely as possible, closed by a tap *S* and weighed; it was then connected to a glass tube *B*, filled with pure metallic copper, also exhausted and weighed; U tubes *C C* containing sulphuric acid on pumice-stone were joined to *B*, and also a tube *D* containing potash. *B* was heated to redness, and the taps *S S S* opened sufficiently to admit a slow current of air. This passed first over the potash, which removed carbon dioxide, next over the sulphuric acid, which absorbed ammonia and water, and then into *B*, where the oxygen was abstracted by the copper. Finally, most of the nitrogen passed into *A*. As soon as air ceased to enter the apparatus the taps were closed, *B* was allowed to cool, and reweighed,

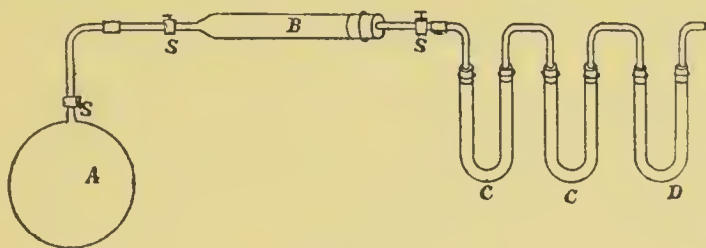


Fig. 42.

first when containing residual nitrogen, and again after the removal of this nitrogen by an air-pump.

By deducting the original weight of *B* and its contents from their weight after the oxidation of the copper, and after removing the nitrogen, the weight of the oxygen taken up by the copper was arrived at.

By finding the weight of *A* when full of nitrogen, and deducting from this its weight when empty, the weight of nitrogen in *A* was found, and by adding to this the weight of the nitrogen which remained in *B*, as determined by the two final weighings of *B*, the total weight of nitrogen was found.

A number of careful experiments made by this method showed that the proportion of oxygen in 100 parts of air varies between 22.99 (in Geneva) and 23.10 (in Brussels).

67. Does air contain a mixture or a compound of oxygen and nitrogen? From an earlier section we have learnt :—

(a) That heat or light, or both, are usually evolved when two or more elements combine.

(b) That the proportions in which two elements unite to form a given compound are fixed.

(c) That whilst the properties of a mixture correspond to those of its constituents, the properties of a compound differ more or less distinctly from those of the substances from which it is formed.

Let us apply these considerations to the case of atmospheric air.

EXPERIMENT 65. (a) To learn if heat or light are evolved when oxygen and nitrogen are mixed in the proportions in which they form atmospheric air. Fix a thermometer *A* in the mouth of a jar (Fig. 43), fill the jar with water, close its open end with a plate of ground glass, stand it in the trough, and introduce nitrogen

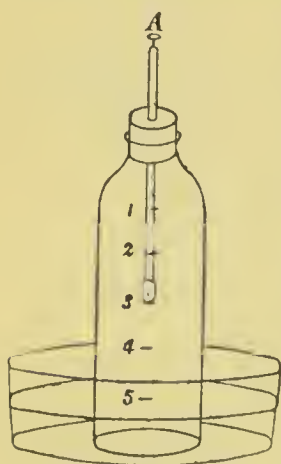


Fig. 43.

to 4. Then fill up with oxygen to 5, and notice, as you mix the gases, whether there is any change of colour, a flash of light, and whether the thermometer is sensibly affected. Remove *A*, introduce a burning taper into the gas, and observe that it burns as in air.

It has been shown by experiments, which we may not repeat, that small animals such as mice can live in a mixture such as that which we have made as well as in atmospheric air.

(b) If you refer to section 66 you will find that, according to the most exact analyses, the composition of atmospheric air is not quite constant.

(c) Consider the properties of oxygen and nitrogen. Is not air like both these gases in its want of colour, taste, and odour, and in its comparatively slight solubility in water? Does not air support combustion in such a degree as you might expect if it were a mixture of a strong supporter of combustion, like oxygen, with a large proportion of a non-supporter of combustion, such as nitrogen?

Finally. If air is shaken up with water, then expelled from the solution (see Expt. 6), collected and analysed, its composition differs from that of atmospheric air, the proportion of each gas corresponding closely to its individual solubility in the free state.

All these facts point to the conclusion that the oxygen and nitrogen in air are not combined.

The above conclusion is supported by the following further considerations:—

(d) That the proportions of oxygen and nitrogen in air do not exhibit any simple relation to their combining weights (see 84).

(e) That the power of absorbing heat possessed by air is about equal to that of oxygen and nitrogen, whilst experience shows that if the two gases were combined in air, its absorbent powers would probably be much greater than those of its components.

(f) The oxygen and nitrogen of air can be separated, to some extent, by diffusion through a porous plate (see 129).

68. The components of air continued. Although oxygen and nitrogen constitute the greater part of atmospheric air they are by no means its only important constituents.

The phenomena of rain, hail and snow show us, for example, that the vapour of water must be present in considerable quantities, and another component of the atmosphere is carbon dioxide.

EXPERIMENT 66. To identify carbon dioxide and to detect it in atmospheric air.

1. Expel air from your lungs for half a minute or so through a glass tube dipped in some lime-water*.

2. Ignite a picce of charcoal in a deflagrating spoon, let it burn for a few minutes in a jar of air or oxygen containing a little lime-water, then close the mouth of the jar with a plate of ground glass and shake up the lime-water with the residual air.

3. Dissolve a bit of marble in some dilute hydrochloric acid in a test tube fitted with a delivery tube, and pass a few bubbles of the gas evolved through lime-water.

From the results of these three experiments you will find that the air from your lungs, the air from burning charcoal, and that set free when marble is dissolved in acid, all yield precipitates when passed into lime-water. The substance which causes this precipitate is carbon dioxide (279).

Now seek carbon dioxide in the atmosphere by drawing a stream of air through lime-water placed in the bend of a U tube. Notice that you obtain a precipitate, but not until a good deal of air has passed through the lime-water.

This is because the proportion present is very small. Pure country air contains about 3.0 c.c. of carbon dioxide in 10,000 c.c. of air, but

* *Limestone*, when ignited, leaves a residue of *quicklime*, this when treated with water gives *slaked lime*, and slaked lime in solution forms *lime-water*. (See calcium, 379.)

the proportion is not quite constant, and a good deal more is present in air collected from near the surface of the earth, or during foggy weather. Air collected from over the sea contains only 3 volumes of carbon dioxide in 10,000, and the proportion does not vary as it does in air collected above the land. In crowded rooms and similar places the proportion is often much higher than is stated above, but it must then be regarded as an impurity.

To measure the proportion of water-vapour and carbon dioxide in the air, a large aspirator provided with two taps (t t') is connected, as shown in Fig. 44, with six U tubes. Of these, 1 and 2 contain strong sulphuric acid, 3 and 4 caustic potash, and 5 and 6 strong sulphuric acid. On opening the taps, water escapes from t , and a corresponding volume of air is drawn through the U tubes. Water and a trace of ammonia are absorbed in 1 and 2, carbon dioxide is absorbed in 3 and 4, any water which may be carried from the potash in 4 is stopped in 5, and the passage of water from A to 5 is prevented by the contents of 6.

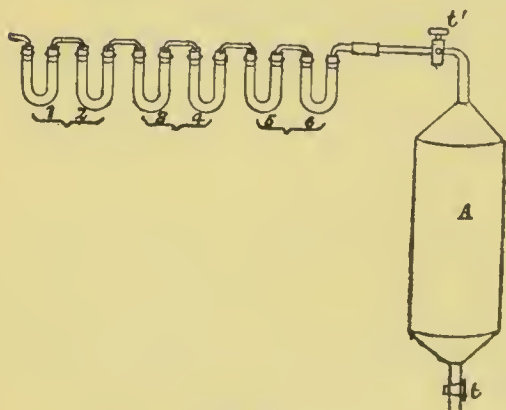


Fig. 44.

ammonia are absorbed in 1 and 2, carbon dioxide is absorbed in 3 and 4, any water which may be carried from the potash in 4 is stopped in 5, and the passage of water from A to 5 is prevented by the contents of 6.

The increase in the weight of 1 and 2, and of 3, 4, and 5 respectively, gives the weight of the water and carbon dioxide collected. The volume

of the water which flows from A gives the volume of the air used, and we can calculate the weight of this air, for a litre of dry air at 760 mm. and 0° weighs 1.293 grams.

The quantity of moisture in the air is greater, as a rule, in hot weather, even when the air seems dry, than in cooler weather when it may possibly seem to be very damp. This is due to the fact that the vapour pressure of water, increases rapidly with increase of temperature (see 23). Consequently, an amount of water which would be sufficient to saturate a given volume of air, and cause it to deposit rain or dew if cooled ever so slightly on a cold day, would be far from sufficient to saturate it in very hot weather. The hygrometric condition of the air is chiefly studied by means of wet and dry bulb thermometers, but it may also be investigated by the chemical method described above.

The other substances usually found in pure air are :—

1. *Ozone*, a peculiar form of oxygen, and *hydrogen peroxide*, in traces (see 124). It is suspected that the salubrity of country air may be due partly to these two components, as they are absent from the air of towns, dwelling-rooms, and crowded places.

2. *Nitric Acid*, or some oxide of nitrogen, which is often, but not invariably, present in small quantities, and may perhaps be produced from the other constituents by electric discharge.

3. *Ammonia*. At a height of two metres from the ground five or six parts of ammonia are present in 1,000,000 of air according to Mr. Horace Brown. It is thence carried to the earth where it contributes to the nourishment of plants.

4. Argon, neon, krypton and xenon have lately been discovered in very small quantities (see 216).

69. Impurities in the air. All the above substances appear to be present in the purest country air, and all, except the last four, are useful either to plants or animals; but when carbon dioxide or ammonia occurs in much more than the normal proportions, it must be regarded as an impurity. Other impurities are organic matter, living organisms, which abound in badly ventilated places, saline matter, and, in the neighbourhood of towns, sulphuric acid from the iron pyrites present in most coal. Several of the less plentiful constituents of the air may be most conveniently detected by examining rain-water.

TABLE OF THE COMPONENTS OF ATMOSPHERIC AIR.

Oxygen	20.65 volumes	
Nitrogen	77.11	„
Argon, &c. . . .	0.8	„ (about)
Carbon dioxide . .	0.03	„ „
Ozone	traces	
Water-vapour . .	1.4	(average)
Ammonia	traces	
Nitric acid	„	
		100.00

If we neglect the other constituents of air, the approximate proportions of oxygen and nitrogen are as follows :—

	<i>By Weight.</i>	<i>By Volume.</i>
Nitrogen (including argon) . . .	77	79.2
Oxygen	23	20.8

70. Incandescence and ignition. When a solid, such as a lump of lime, is strongly heated, its temperature gradually rises until at length it emits light, becoming, as we say, 'red hot,' or at a higher temperature, 'white hot.' Substances in this state are said to be ignited or incandescent. If the external source of heat be withdrawn, the temperature of the substance falls, and it soon loses its luminosity.

When a substance is ignited it may or may not acquire new properties. Lime, for example, remains unchanged at an intense heat, but limestone * is converted into 'lime' when similarly treated, as will be found from the following experiment.

EXPERIMENT 67. To study the effect of heat on limestone. Heat a weighed quantity (about 2 grams) of marble, in small pieces, for some time in an open crucible, to a very high temperature in a furnace †, and reweigh the residue, after allowing it to cool in a desiccator.

If you repeat the process until the lime ceases to lose weight, you will find that 100 parts of limestone yield only 56 parts of lime; and if you then slake a fragment of the lime, by adding a little water, and dissolve the product in dilute acid, you will find that it no longer gives off carbon dioxide like unheated marble (see 279, 2), for limestone, when heated, is decomposed into 56 per cent. of lime and 44 per cent. of carbonic acid gas which escapes.

71. Combustion. When we heat magnesium the phenomena are different, in several respects, to those last studied. At a certain temperature a violent *evolution of heat* sets in, and the metal is quickly converted into a white non-metallic powder which weighs more than the metal taken to produce it. Similarly, if we warm a fragment of phosphorus to 45° , and then quickly remove the source of heat, the phosphorus does not cool down like incandescent lime, but continues to emit light and heat until all the element is replaced by a new substance, which we shall study subsequently. These are examples of *combustion* or *burning*.

In the majority of the more familiar cases of combustion the substance burnt unites with the oxygen of the air, but the use of the term need not be restricted to phenomena of this class. Indeed, in its

* The term 'limestone' is applied to a number of minerals, such as chalk and marble, which yield lime when ignited. Though differing in origin and appearance they all have similar composition. (See calcium carbonate, 384.)

† Fletcher's oxygen furnace is suitable for this experiment. But it must not be used at its full power.

widest application it may be applied to any chemical change in which the acting substances become luminous owing to heat liberated in the course of the change. In what follows, however, only ordinary cases of combustion in air will be discussed.

72. Combustible substances, supporters of combustion, and inverted combustion. It is natural to draw a distinction between combustible substances, such as wood and hydrogen, and supporters of combustion, such as air and oxygen. But since the thing burnt and the supporter of combustion appear each to combine with the other, it seems probable that they would still combine if their positions were reversed. That is to say, for example, it seems likely that a jet of air would burn in a room filled with coal gas or hydrogen, as readily as a jet of coal gas or hydrogen burns in a room containing air. Let us see if this is the case.

EXPERIMENT 68. To burn a jet of air in an atmosphere of coal gas. To the wider mouth of a tube *A* (Fig. 45), fit a cork carrying a tube *C*, and a short and rather wider tube *D*. Insert a slightly smaller tube *E* in *D*, securing it by means of an india-rubber cap at *F*. Connect *E* with a gas-holder filled with air; and place a tube *G* made of a bit of mica, or of asbestos paper, loosely in the narrow end of *A*. Connect *C* with the gas supply pipe, turn on the gas, and light it at *G*. Then raise the end *H* of *E* to *G*, and allow a gentle stream of air to enter into the burning gas, and when the air catches fire lower *E*. You will then see a jet of air burning with a pale blue flame in an atmosphere of coal gas.

But although air burns in coal gas as readily as coal gas burns in air, you will notice that whilst the flame of coal gas at *G* is luminous, the flame of burning air at *H* is non-luminous. This difference reminds us of the fact, that the conditions under which the two gases are burnt are not the same. At *H*, we have air surrounded by an excess of coal gas; at *G* we have gas surrounded by an excess of air. At *G*, therefore, the gas is likely to be completely oxidized; at *H* it is quite likely to be incompletely burnt, owing to the relatively small supply of oxygen available. If instead of coal gas we used hydrogen

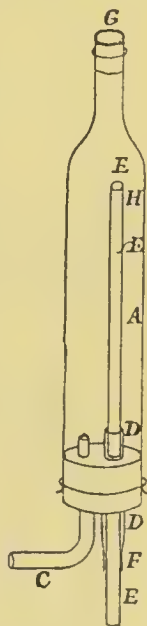


Fig. 45.

this would make no difference in the chemistry of the phenomena, for

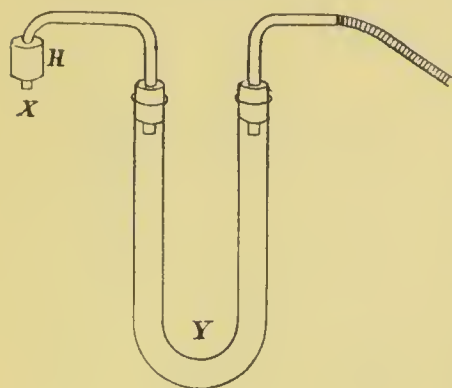


Fig. 46

then water, and water only, would be produced, both at *H* and *G*. But as coal gas is a mixture of several substances (see 303), it is clear that at *H* we may be burning only one or two of its constituents and leaving the others unconsumed, whilst at *G* all are likely to be burnt. To test this hypothesis, a sample of the gas used and a sample of that which issues from *G* might be collected and analysed; but work of this kind takes much time and can

only be performed by an accomplished experimenter.

73. The structure of a flame. When anything burns in air it may happen, as in the case of magnesium, that the product is a solid; but often, as in the case of coal gas, hydrogen, oil, and wax, the substances produced are partly or wholly gaseous. In this latter case we obtain 'a flame,' which consists essentially of a mass of intensely ignited gaseous matter. If you compare the flames of various combustible substances, you will find that some, like hydrogen and carbon monoxide, give non-luminous flames, and others, which are rich in carbon like oil and wax, give flames which are luminous. To ascertain the cause of this luminosity we may study the flame of a candle.

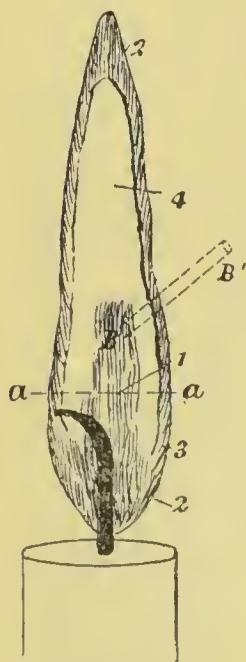


Fig. 47.

EXPERIMENT 69. Study of a candle flame.

1. Place a burning candle in *A* (Fig. 45), after removing *E*, and attach a U tube *Y* (Fig. 46), by a cork *H* at *G*. Then draw air through the apparatus, first when *Y* is empty, and again after introducing some lime-water. You will find that water and carbon dioxide are produced, together, perhaps, with a little unburnt carbon.

2. Remove the candle from *A*, and depress a cold plate upon its flame. Note that a copious deposit of solid carbon forms on the plate, and that this seems to come most plentifully from the luminous parts of the flame.

3. Hold a splinter of wood across the flame, along the line *aa* (Fig. 47), and notice that it is quickly charred at the edges of the flame, but not in the dark central portions.

4. Place a narrow glass tube in the position of the dotted lines *BB'*. If you do this skilfully gases will issue at *B'*, which will burn if you apply a light to them.

5. Extinguish the candle, and notice that vapours arise from its wick. Gradually bring a lighted taper towards these vapours; they will catch fire and relight the candle long before the flame of the taper reaches the wick itself.

6. Melt some tallow or wax in a dish, and introduce one end of a lamp wick into the melted grease. Notice that the oil climbs some distance up that part of the wick which is not immersed in the oil.

7. Heat some tallow in a test tube *A*, provided with a jet *B* (Fig. 48), till fumes escape, and apply a light to the fumes. They will burn like the fumes given off from the candle wick in 5.

If you carefully observe the flame of a burning candle, you will see that the wick is surrounded by a dark region or zone 1 (Fig. 47), which consists, as we have already ascertained, of combustible gases resembling those given off by strongly heated grease. This part of the flame is not sufficiently hot to char wood, and from the results of 6 and 7 it seems clear that its combustible constituents are formed from melted grease, which has run up the wick and been decomposed by the heat of the surrounding parts of the flame.



Fig. 48.

Near the base of the flame at 2 it is easy to distinguish a bright blue region, which gradually shades off into a barely visible zone or mantle, 3, which surrounds the whole flame. Finally, between the zone of unburnt vapour, 1, and the mantle, 3, there is an extensive and highly luminous zone, 4, which is evidently the chief source of the light of the flame. Now we have found (2) that the luminous zone deposits unburnt carbon plentifully when it is cooled; therefore in this zone the combustion must be incomplete, and 4 is accordingly called the zone of incomplete combustion. On the other hand, the mantle and the base of the flame, which consist mainly of water-vapour and carbon dioxide (see 279), may be termed the zone of complete combustion. Thus it would seem that, broadly speaking, a candle flame consists of three main parts or zones:—

A. A space round the wick filled with gases produced by the decomposition of the grease.

B. A middle or luminous zone of incomplete combustion.

C. The basic portion and the mantle, which consists mainly of strongly ignited water-vapour, carbon dioxide, and nitrogen.

The flames of coal gas and of oil lamps will be found, on examination, to consist of similar parts, similarly distributed.

74. Why some flames are luminous. It has previously been pointed out that, under ordinary circumstances, luminous flames are produced by substances which are comparatively rich in carbon, and that the flames of such substances as hydrogen, carbon monoxide, sulphur and marsh gas are not luminous, except under special conditions. Further, we have seen that the luminous zones of light-giving flames readily deposit solid carbon. Hence it may be supposed that these flames owe their luminosity to the presence in them of swarms of minute particles of highly ignited carbon. This hypothesis is supported by various facts. Thus :—

1. If you examine the light from a luminous flame and also that of a strongly ignited solid, such as a crucible made white hot, with a spectroscope, you will find that both give a continuous band of light. Now an incandescent gas gives an entirely different spectrum (see 336); hence the presence of solid particles in a luminous flame seems probable, and carbon is the only solid likely to occur in the flames of substances composed of hydrogen and carbon, such as paraffin oil or wax.

2. A luminous flame is more opaque than one which is non-luminous.

3. Luminous flames become non-luminous if air or oxygen is injected into them (see Bunsen burner, 75).

4. Non-luminous flames can be made luminous by introducing solid carbon or other solid matter, even if it be incombustible.

The origin of the carbon in luminous flames has been the subject of many discussions. At one time it was supposed that when compounds rich in carbon are burnt with a deficient supply of oxygen, such as may be imagined to occur in the luminous zone of a flame, the hydrogen is consumed completely, but that much of the carbon is left unburnt. In the face of recent discoveries this idea can no longer be adopted. The older students will do well to read what has been written on flames in one of the larger treatises on Chemistry

but before the subject is dismissed the following facts may be mentioned.

1. Luminous flames may be produced under circumstances which do not support the idea that solid matter is always present in such flames. Thus the flames of burning phosphorus and arsenic are intensely luminous. Yet the oxides of phosphorus and arsenic are volatile at the temperatures of these flames.

2. When a mixture of nitric oxide and carbon disulphide is ignited no solid matter separates, but the flame is highly luminous.

3. Oxygen and hydrogen exploded under pressure give a bright light, though the same gases burnt at ordinary pressure give but little light.

The late Dr. Frankland suggested that the luminosity of the flames produced by such substances as phosphorus and arsenic may be connected with the densities of the vapours formed; and the effect of pressure on the luminosity of burning hydrogen (see 3, above) and alcohol, and on the character of their spectra (336), suggests that the luminosity of hydrocarbon flames may possibly be due to the presence of dense hydrocarbons. At present, however, it is generally held that in these latter cases luminosity depends, as stated before, on the presence of clouds of minute particles of ignited solid carbon in the luminous parts of the flames.

75. The Bunsen burner. This form of gas burner was contrived more than thirty years ago by Baron Bunsen. It consists of a tube *E* and a chamber *A* (Fig. 49), provided with one or more openings *D*. When gas is admitted by *C* to the jet *J*, it creates an area of low pressure, and thus sucks in air through *D*; consequently a mixture of air and gas escapes at *E*, where it burns with a clear smokeless flame.

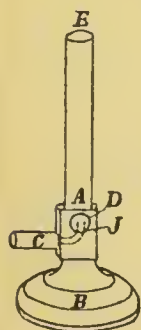


Fig. 49.

If you examine the flame of a Bunsen burner closely you will find that it consists of two well-defined cones. These can be easily studied by means of Professor Smithell's separator (Fig. 50).

Air and a combustible gas are admitted separately by the two limbs *A* and *B* of a T tube to *C*, which is fixed in a larger tube *D* by an india-rubber joint at *E*. Thin sheets

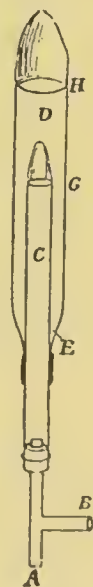


Fig. 50.

of mica, bent into cylinders, are inserted at *H* and *G* so that the burning gases may not come into contact with the glass.

If air and gas be admitted to this apparatus at a suitable pressure and ignited at *H*, a non-luminous two-zoned flame will form there. If then the supply of gas and air are carefully regulated the inner cone can be made to travel down *D* and burn independently at *G*. The gases in the space *H G* can be drawn off and analysed. They have been found to contain elementary hydrogen as well as oxides of carbon, thus showing that the assumption alluded to on p. 88 had no foundation in fact.

INFLUENCE OF THE LIFE PROCESSES OF ANIMALS AND VEGETABLES ON THE COMPOSITION OF ATMOSPHERIC AIR AND UPON THE SURFACE SOIL.

76. Constancy of the composition of the air. We have learnt that the composition of country air, taken from different places, is not so constant as that of a chemical compound. On the other hand, as far as we can judge, the proportions of oxygen, nitrogen, and carbon dioxide in the air to-day do not differ greatly from those present a thousand years ago. Therefore when we consider that every animal must render a very large volume of air unfit for respiration* during its lifetime, and remember that countless generations of animals have

successively flourished in a quantity of air which, though considerable, is nevertheless limited in quantity, it is natural to conclude that there must be a recuperative process, and to seek to learn its nature.

Both atmospheric air and the breath of animals contain carbon dioxide (68). Let us first compare the proportions of this gas present in pure air and in the breath of an animal.

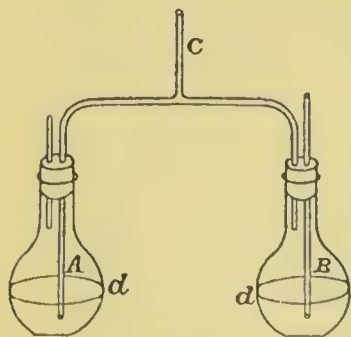


Fig. 51.

EXPERIMENT 70. To compare the amount of carbon dioxide in air before and after respiration. Fit up the apparatus shown in Fig. 51; place lime-water to the line *d d* in the flasks. Attach an india-rubber tube to *C*, and breathe through the apparatus by means of this tube. You will find that

* An animal cannot long exist in the same air if its quantity be limited.

when you draw air into your lungs it enters through the lime-water in *B*, and that when you expel the air it escapes through that in *A*. Before long you will see that the lime-water in *A* becomes milky, whilst that in *B* still remains clear, showing plainly that the air from your lungs contains more carbon dioxide than the atmosphere. Let us next measure the carbon dioxide in expired air, and try to learn if it is produced at the cost of another constituent.

EXPERIMENT 71. To measure the volumes of oxygen, nitrogen, and carbonic acid gas in respired air. Introduce about 50 c.c. of air from your lungs into a eudiometer (Fig. 41), taking the last portions expired, and measure its volume. Treat it with strong solution of potash in the gas pipette to extract the carbon dioxide and re-measure it. Then ascertain the proportion of oxygen in the residuc by means of pyrogallic acid (Expt. 62), and set out your results in a table. On comparing the composition of respired air with that of pure air (Table, p. 83), you will find that respired air contains less oxygen in proportion to the nitrogen, and more carbon dioxide than unrespired air. This explains why respired air is unwholesome. It is first, because each time the same air is inhaled the supply of oxygen is diminished, and secondly, because the oxygen removed is replaced by carbon dioxide, which is well known to be unwholesome except in very small quantities. Therefore if an animal remains for long in a confined space he gradually consumes the oxygen till too little remains to support life, and at the same time introduces into the air a dangerous quantity of unwholesome carbon dioxide.

But carbon dioxide does not come into the air solely from the respiration of animals. Much is produced by the burning of carbon, in the form of coal (279, 1), and of substances containing carbon, such as peat, wood, and oil, and much by the decay of the remains of plants and animals, whilst still more * issues from subterranean sources. The supplies derived from these various sources are so great that it has been calculated the proportion of carbon dioxide in the air would be more than doubled once in every four centuries if no causes of diminution existed.

The following experiment will help us to understand the nature of the process of purification.

77. Influence of plants on the atmosphere. **EXPERIMENT 72.** To learn whether gases are given off by plants. You may very

* It is said ten times as much

possibly have observed, at some time or another, the bubbles which form upon the leaves of plants growing under water. If not, expose a young and growing plant to direct sunlight under water at the temperature of the air, or better, tie some common water-plant, such as one of the pond-weeds, to a stone, plunge it under water in a deep vessel and expose it to the sun. In either case bubbles will soon form on the under-surfaces of the leaves, which may be collected easily by means of such an arrangement as that shown in Fig. 52. If you examine some of this gas by the usual tests, you will find it ignites a glowing match, for it consists largely of oxygen.

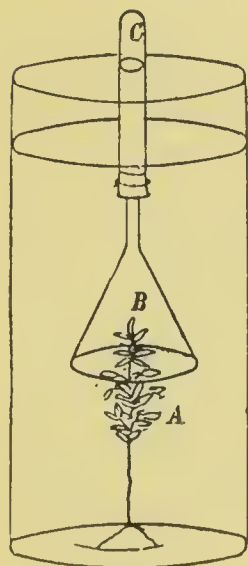


Fig. 52.

From the last experiment we learn that whilst the oxygen in the air is constantly diminished by animal life, decay, and combustion, the supply is constantly renewed by the plants. We cannot, of course, measure the total consumption of oxygen nor the amount supplied by plants, but it is certain that if the former be great the latter must also be very large and go far to compensate the constant drain. But plants not only supply the air with oxygen, they also consume carbon dioxide. When Her Majesty Queen Victoria ascended her throne most people believed that plants, like animals, feed mainly on organic matter. They were supposed to extract this matter from the 'humus' of the soil*, until Liebig abruptly demolished the 'humus theory' in 1840, by showing it to be practically impossible that the plants could absorb 'humus,' which is nearly

insoluble, and made it clear that they really feed mainly upon inorganic substances such as carbon dioxide, nitric acid, water, lime, and potash, and that they obtain their carbon in particular from the carbon dioxide of the air, which they separate into carbon and oxygen, retaining the former but returning the latter to the air for the use of animals†.

It is impossible to find space here for more than a few very general statements on the chemistry of plant life, but it may be said that the changes by which a continual circulation of oxygen and carbon between plants and animals is maintained appear to depend upon the

* Humus is the earthy matter formed by plants in the process of decay.

† It appears that carbon dioxide is also withdrawn from the air by certain chemical changes which take place on its surface, such as those in which felspar is changed into clay (see 310).

agency of the green parts of plants, and to be in some way connected with the action of a green substance called *chlorophyll*. Numerous analyses show that plants are composed chiefly of carbon, hydrogen, and oxygen, together with nitrogen, sulphur, phosphorus, and mineral matter in very much smaller quantities. Their carbon is derived, as we have learnt, from carbon dioxide, and their hydrogen is believed to be absorbed, chiefly by their roots, as water, together with mineral matter which it holds in solution. It was at one time supposed that plants obtain their nitrogen, which is especially important for the production of seeds, solely in the form of ammonia and nitric acid from the soil, but it has lately been discovered that members of the pea tribe, in association with certain micro-organisms, are capable of assimilating the nitrogen of the air.

You will now understand that plants prepare the way for animals by elaborating from inorganic* materials the organic substances on which the latter chiefly subsist, and that in doing so they remove from the air the carbon dioxide which is introduced by animals and other agencies, and also continually renew the supply of oxygen.

Animals, on the other hand, consume the organic substances elaborated by plants, resolving them again into simpler substances such as carbon dioxide and ammonia†, and continually use up the oxygen liberated by the plants. In short, the life processes of plants prepare the way for those of the animals, and thus make it possible for a limited store of carbon, oxygen, and hydrogen to support the existence of countless generations of both.

78. Animals and nitrogen. It was stated in the last section that the tissues of plants are composed of carbon, hydrogen, and oxygen, with small quantities of such elements as nitrogen, sulphur, phosphorus, and some saline matter. The tissues of animals also contain much carbon, hydrogen, and oxygen, but they are distinguished from those of plants by the presence in them of much larger proportions of nitrogen, and sometimes by the presence of considerable amounts of mineral matter. Animals obtain these things with the other components of their food, through the action of the stomach, from which, after they have been dissolved, they are transmitted, partly by the blood, to all portions of the body to play their parts in

* Compounds of carbon other than a few of the more simple ones are called organic compounds, because it was thought at one time that they could only be produced in the organized structures of plants and animals.

† Ammonia is composed of nitrogen and hydrogen (see 217), and is produced by the decay of animal matter.

the chemical changes on which the life of each animal partly depends. The waste products are afterwards removed and excreted, the carbon as carbon dioxide, the nitrogen, in the case of the higher animals, in the form of a compound called urea, which is composed of nitrogen, hydrogen, oxygen, and carbon (see also 306).

79. Decay. The decay which follows the death of a plant or animal, and in which much carbon dioxide is formed, was at one time considered to be a slow kind of burning, but it is now recognized, largely through the researches of Pasteur (b. 1822, d. 1895), that this process really depends on the existence of minute organisms, which feed as it were on the dead material, gradually resolving it into products of oxidation. If organic matter be heated sufficiently to kill these organisms and afterwards protected from the approach of fresh ones, it may be preserved from decay indefinitely. The carbon dioxide produced in decay may therefore be classed with that formed in the life processes of the higher animals.

FURTHER EXERCISES ON PART I.

Before proceeding further, the student will do well to perform as many of the following additional exercises as the time at his disposal may permit. The order in which they are taken is not very important, e.g. those on crystallizing, G, H, &c., might possibly in some cases precede those on dissolving, A, B, &c., with advantage.

As nearly all these additional experiments are more or less similar in their main features to experiments previously performed by those who use this book, they are described in outline only. This will not only save time, but, by encouraging the student to recall his past work, will help him to develop his mental powers, and so be more truly helpful than fuller instructions would be at this stage.

Before doing each experiment, read and re-read the instructions to the end. Do not begin to work till you understand them and feel sure you can carry the experiment through with the book closed. Unless you do your best to follow this instruction the work will not be very profitable. You may find, at first, that, after doing your best, you must consult the book now and then after you have begun to work.

When this happens read the whole again, so that you may afterwards be able to carry the experiment through without again reading the instructions. If you follow this advice you will not only learn more of your subject, but also strengthen your memory considerably in a few months.

EXERCISES ON SOLUBILITY.

EXERCISE A. To find how much of a solid is dissolved in a solution. Obtain a saturated solution of common salt from your teacher, or prepare some by shaking *finely powdered* salt with twice its weight of cold water for ten minutes or so.

Obtain a small evaporating basin with a short glass rod, and weigh the dish with the rod. Pour 5 or 6 c.c. of the solution into the dish and evaporate it, taking care that no loss occurs through spurting. To avoid spurting, do not evaporate too quickly, and stir the residue diligently when the salt begins to form, especially when you have a pasty mass of damp salt in the dish.

When the salt is quite dry let it cool in a desiccator, Fig. 21, p. 37 (32*). Then weigh the dish and its contents. To make sure all the water is expelled from the salt, re-heat it for a few minutes and re-weigh it.

Now set out the results obtained in your note-book in a similar form to those given on p. 36 (31), stating at the end how much salt you find dissolved in each 100 grams of water.

This experiment should be repeated once or twice, using other solids, e.g. sodium sulphate, potassium sulphate, sugar, or washing soda, till accurate results are obtained.

Substances, like sugar, which are liable to be damaged by heat must be dried in an air bath or on a water bath. The solubility of one such substance, at least, should be studied.

Note.—In every case ascertain from your teacher how nearly your results agree with those obtained by more experienced workers.

EXERCISE B. To find quantitatively whether heat affects the solubility of salts.

1. Repeat the above experiment, using a solution of salt made by shaking salt and water together at 60°, and compare the result with that obtained in Exercise A.

2. Make similar experiments at the temperature of the air and at 50° with nitre.

3. Those who have time should make a third set of experiments, using sodium sulphate, first at the air temperature, and also at 100°. Other experi-

* References in brackets given in the directions for these Exercises refer to the *Laboratory Companion*.

ments might be made with washing soda or copper sulphate by those who have ample time at their disposal.

Now state whether you find any evidence that solids as a rule are more soluble in hot water than in cold, or more soluble in cold water than in hot.

EXERCISE C.—To separate substances from mixtures by means of solvents. Get from your teacher a mixture of two such substances as sand and salt in known proportions, or prepare a mixture by mixing thoroughly in a mortar weighed quantities of the two solids.

Place two or three grams of this mixture in a flask or beaker of known weight. Add hot water and shake the mixture and the water together for a few minutes.

Place two folded filter papers of similar size one inside the other in a funnel. Decant the liquid contents of the flask into the filters, taking care to spill none. Treat the remaining sand with a little more hot water, decanting the solution through the filters as before, and repeat the process two or three times.

Now wash all the sand on to the filter. Wash the sand and the filter paper carefully with hot water to remove all salt. Finally, dry the filter papers; place that with the sand upon it on one pan of the balance and the clean filter paper on the other pan. Find the difference by weighing.

Finally, state how much sand and how much salt you have found in every 100 parts of the mixture.

Notes on the above.—1. For washing the filters use a wash bottle. You can ask your teacher what this is if you do not know.

2. If the insoluble constituent of the mixture is very heavy and settles perfectly and quickly, you may simply wash it repeatedly with hot water, dry it in the flask, and weigh it. Ask your teacher how to dry a flask before you attempt this.

Questions.—1. How can you make sure that your filters are thoroughly washed?

2. How could you vary the experiment so as to find the composition of the mixture without weighing the sand?

3. How could you *confirm* the result obtained by either process?

You must on no account proceed further till you have answered these questions or discussed them with your teacher.

EXERCISE D. Make experiments similar to the last, using other mixtures, e.g. salt and iron rust, chalk and washing soda, if time permits.

EXERCISE E. To find the strength of an acid by studying its solvent power. Weigh out about 10 grams of marble in small fragments. Pour upon them 10 c.c. of solution of hydrochloric acid containing about 5 per cent. of hydrochloric acid. Leave the acid on the marble till visible action ceases. Decant the liquid, wash the residue of marble repeatedly with distilled water, dry what remains and weigh it.

Now repeat the experiment, using some solution of hydrochloric acid of unknown strength, and from the amounts of marble dissolved in the two cases calculate the strength of the latter acid.

N.B. State all your results clearly in tabular form as in previous cases.

EXERCISE F. Find if plaster of Paris, slaked lime, barium sulphate and chalk, are soluble in water.

Remember that you will not be able to discover this by merely shaking them with the water and observing the result with your eyes, unless they are very soluble.

If you omitted **Experiment 33**, p. 40 (36), or succeeded ill with it, it would be well now to perform this experiment.

A more exact method of finding solubilities for the use of older students will be found on p. 35 (31). Before proceeding, you should study the solubility curves given on p. 36 (32) and also those in the table at the end of the book, and make sure you understand their meaning.

EXERCISES ON CRYSTALLIZING, AND ON PREPARING SALTS BY THE ACTION OF ACIDS ON ALKALIS OR METALS.

Look over your notes on Crystallizing or re-read this subject on pages 38-42 (34-38).

EXERCISE G. To extract pure table salt from rock salt.

Crush some rock salt. Extract as much of the salt as you can by means of water from 100 grams or so of the mineral. Filter the solution, and evaporate it until a sufficient deposit of crystals has formed. Collect these on a filter, wash them with a little water, drain and dry them.

Repeat the process if the salt is not yet pure.

Salt thus prepared contains, usually, a little bromide of magnesium. This causes the salt to become moist in damp air. To obtain really pure salt, dissolve as much table salt as you can in 30 c.c. of cold water and filter. Then add 30 c.c. of strong hydrochloric acid to the solution. Let the sediment of salt settle. Decant the 'mother liquor.' Wash the salt in the dish with a very little strong hydrochloric acid, drain it, and dry it by heating gently. It will now be free from the bromide.

Many other solids may be crystallized as well as salts. For example, sugar. Sulphuric acid slightly diluted and well cooled yields very attractive-looking crystals, which melt in a warm room. Again, metals crystallize, and if you ask your master he will probably be able to show you the beautiful crystals formed by bismuth when it is treated as you treated sulphur in Experiment 30.

EXERCISE H. To prepare crystals of the metals.

Dissolve four or five grams of tin in a little strong hydrochloric acid and dilute the solution with several times its volume of water, or obtain some solution of tin chloride if any is at hand.

Hang a rod of zinc of known weight in the solution of tin, and observe what happens. After an hour or so collect the crystalline deposit of tin, clean and dry the zinc and re-weigh it.

Question. Can you offer any explanation of the result you obtain? If not, consult your teacher.

Try a similar experiment to the last, using a solution of sugar of lead. Sugar of lead is a sweetish, very *poisonous* solid, made by dissolving oxide of lead in white vinegar, i. e. acetic acid.

Try another experiment, using a solution of copper sulphate.

Try if iron or magnesium will act in a similar manner on solutions of the above salts.

Try if tin will displace copper from a solution of copper sulphate. Try also solutions containing other salts of copper.

Try whether zinc will displace crystals of silver from a solution by placing a bit of zinc as big as a mustard seed in a drop or two of solution of silver in nitric acid (silver nitrate), and observing the result with a lens or under a microscope. To get a good result, the solution of silver nitrate should be made slightly acid with nitric acid.

Precipitation. Examples of precipitation will be found on p. 139 (80), Exp. 83.

EXERCISE J. To prepare salts by dissolving metals &c. in acids and producing crystals from the solutions.

1. Add about five cubic centimetres of sulphuric acid to about 40 c.c. of water; then add 10 grams of iron turnings to the liquid in a basin. Notice the signs of action which at once show themselves. When these cease, decant or filter off the solution, evaporate it on a sand bath to about one-fourth of its original volume or till crystals begin to separate. Then set it aside to cool.

Compare the solid thus obtained with iron turnings, and say whether the dissolving of iron is a case of chemical or physical change (see chap. iii).

2. Make a similar experiment to the above, but substitute zinc for iron.

3. Make another similar experiment, using copper and 10 c.c. of nitric acid diluted with three or four times its volume of water. Note how the gas evolved in this case differs from that evolved in 1 and 2.

4. Make a similar experiment, using marble and hydrochloric acid. In this case boil down the solution till a solid residuc remains.

Leave some of this residuc exposed to the air on a dish for a day or two, and observe the result.

5. If you are skilful, you can obtain tin chloride in crystals by dissolving tin in hydrochloric acid and concentrating the solution till it crystallizes on cooling.

6. Try to obtain crystals of silver nitrate from a scrap of silver.

7. Dissolve 20 grams or so of slaked lime in strong hydrochloric acid diluted with twice its volume of water. Concentrate the solution to a thick syrup, and leave it in a desiccator that crystals may form.

8. Make a similar experiment, but use about 40 grams of limestone (marble, chalk, pearl, coral, Bath stone, oyster shell, &c.) instead of lime, and nitric acid.

9. Make neutral salts in crystals from sulphuric acid, hydrochloric acid, nitric acid, by neutralizing each with soda, potash, washing soda, or potassium carbonate.

The method is to place either the acid or the alkali diluted with water in a dish and to add the other constituent very gradually, testing the liquid from time to time by placing minute drops from the end of a glass rod on pieces of litmus paper till it is neutral (see p. 146).

N.B.—Do not put the litmus in the solution. You do not want litmus in the salt.

10. Try to make zinc sulphate, lead nitrate, and other salts by shaking oxide of zinc with sulphuric acid, oxide of lead with nitric acid, slaked lime with hydrochloric acid till the acid is neutralized. Then filter off the solution and evaporate to obtain crystals.

11. **Insoluble salts.** Try to make lead chloride by dissolving lead oxide in cold hydrochloric acid diluted with water. If you fail, ask your teacher to explain this. Then try to prepare lead chloride by mixing a solution of lead nitrate with a solution of common salt. Re-crystallize the salt from hot water.

Further work in this direction may be postponed.

PREPARING GASES.

We have seen that liquids may be separated from one another by distilling (see p. 24), and solids by dissolving and crystallizing. It remains to consider the methods of preparing and collecting gases such as Oxygen, Hydrogen, Nitrogen. For this purpose the student will do well to perform the following experiments, selected from Part III, at this stage:—

EXERCISE K. Prepare oxygen as described in Experiment 39, p. 49 (44), if you have not previously done so, and make the following observations on its properties:—

1. Place fragments of wood, carbon, phosphorus, or sulphur, previously ignited, in deflagrating spoons in the gas, and observe the result (see Experiment 60). Let a jet of oxygen play on zinc or magnesium strongly heated in a crucible or on a bundle of fine iron wires heated to bright redness.

2. Prepare the same gas by heating potassium chlorate in *A*.

EXERCISE L. 1. Prepare hydrogen from zinc or iron and sulphuric acid, as described in Experiment 40, p. 49 (44).

Try whether hydrogen supports combustion as oxygen does.

Draw the gases from a jet of burning hydrogen through a well-cooled tube (Fig. 30), and ascertain whether the liquid you collect, if any, is water.

Place jars of hydrogen without glass plates over their mouths upon the table, some with their mouths upward, others mouth downwards. Afterwards ascertain whether they still contain hydrogen.

Try similar experiments with oxygen, and from your results decide which is the lighter gas of the two.

2. Prepare hydrogen from water by means of sodium. Fit up a very small flask or two-necked bottle, as shown in Fig. 28, p. 50. Place in it a little sodium amalgam, prepared by adding sodium to quicksilver warmed in a dish. Then pour some water upon it, and collect the gas as before. The residue of quicksilver should be carefully preserved and given back to the storekeeper.

The watery contents of the vessel *A* should be examined. If they are alkaline to litmus the student should find whether they yield a salt when neutralized with hydrochloric acid.

Oxygen and hydrogen may also be prepared by electrolysis, see p. 44 (40), (Fig. 25).

Hydrogen may be prepared from steam by the action of iron as described in Experiment 52 (p. 59).

EXERCISE M. Nitrogen is one of the constituents of the air. It is left when the oxygen is extracted by means of copper, Exp. 60, p. 71 (55). This experiment should be performed if suitable apparatus is available. And the nitrogen should be examined to learn if it is heavier or lighter than hydrogen, and whether it supports combustion.

EXERCISE N. To prepare carbonic acid gas or carbon dioxide.

Carbonic acid gas may be made by the action of marble on diluted hydrochloric acid, following the method described for making hydrogen on p. 49.

It may also be made by heating a bicarbonate strongly in tube (Fig. 27, p. 49). The student should prepare some of this gas and study its effect on lime-water. Also collect some and discover if it is soluble in potash or soda, and its action on a flame.

He should also pass some of the gas through distilled water holding a little chalk in suspension, then filter off the liquid, test it for hardness, p. 11 (8), and afterwards try if the hardness so produced can be destroyed by boiling.

He may also pass this gas slowly through a strong solution of potash in a U tube till crystals of potassium bicarbonate are deposited.

ACTION OF HEAT.

Water of crystallization. Further experience in determining the water in crystals should be gained by finding whether sodium sulphate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), and magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) yield the quantities of water indicated by the above formula. For the method to be employed see p. 57 (49).

EXERCISE O. Action of heat on common substances.

1. Heat small portions of a few salts such as copper nitrate and sulphate, lead nitrate, zinc carbonate, calcium carbonate (limestone), mercury iodide, ammonium nitrate and phosphate, or the mineral magnesite, in glass tubes or crucibles, first gently, then very strongly in air, first by means of a bunsen burner, then in a furnace.

Observe whether any recognizable gas or vapour is evolved.

Observe whether there is a gain or loss of weight.

Ascertain whether the residues are soluble or alkaline, and whether they neutralize dilute acids and yield salts. When you do this, study the action of the unheated solid on dilute acid also, and take note of any difference you may observe.

Make similar experiments, using potassium tartrate, sugar, gum arabic, starch, and describe the results you obtain with these, especially noting if they give evidence of containing any element you are well acquainted with.

Ascertain if other nitrates and carbonates, and organic substances, e.g. cheese, feathers, cotton, or silk, behave like those first studied, and point out how you may detect such classes of substance on future occasions by the action of heat upon them.

2. Compare the behaviour of sodium carbonate and bicarbonate when heated, with the object of ascertaining whether either of them gives off carbonic acid gas.

3. Experiment 4, p. 3 (4), should be repeated if the student has forgotten it.

4. The student should endeavour to ascertain if the wax of a candle takes up anything from the air in burning, asking his teacher how this subject can be investigated.

EXERCISE P. 1. Repeat Experiment 1, p. 2 (4). Ascertain how much is gained by each gram of magnesium burnt, and, from your result, calculate how much magnesium would combine with 8 grams of oxygen.

Find whether the residue left by burnt magnesium is acid or alkaline to litmus, and whether a little of it will neutralize a few drops of dilute sulphuric or hydrochloric acid. If so, prepare crystals of the product of their combination.

2. Burn carbon and sulphur respectively held in deflagrating spoons in cylinders containing air. Shake up the contents of the cylinders with a little

water, and test the solutions so obtained with litmus to find if the oxides produced are acid or alkaline.

Make similar experiments upon fragments of sodium, potassium, and phosphorus in jars of air, or in tubes in currents of air, and examine the action of the oxides these produce on litmus.

3. Draw up a list classifying the elements carbon, sulphur, phosphorus, sodium, and potassium according to the character of the oxides they form.

4. Ascertain whether any gain in weight occurs when you burn carbon. This may be done by heating a known mass of the element in the tube *E* (Fig. 32, p. 60) (52), in current of air, or with oxygen, and passing the gaseous products slowly through a strong solution of alkali on pumice stone in *G*.

5. Try whether salts such as iron sulphate can be converted into oxides by heating them strongly. Ascertain if they lose weight. Observe whether any gas or vapour is evolved, if so whether the vapour is acid or alkaline, what its colour is and so on, and find if the residues are alkaline, i.e. will destroy acids.

Iron sulphate, copper sulphate, potassium sulphate, zinc nitrate, copper carbonate, calcium nitrate, barium nitrate, may be selected for this experiment.

PART II

THE LAWS OF COMBINATION AND THE ATOMIC THEORY, ETC.

CHAPTER VIII

THE LAWS OF COMBINATION AND THE ATOMIC THEORY

80. The laws of chemical combination continued. We have become acquainted already with several of the chief laws of combination. It will be convenient to restate these before we study the other chief laws of chemistry.

I. **The principle of the conservation of matter, or of the conservation of mass.** *The quantity of matter which takes part in a chemical change remains unaltered when that change is completed,* or as it is sometimes expressed, we cannot create nor destroy a single particle of matter, we can only alter its form.

II. **The law of constant composition.** *A given compound always contains the same elements in the same proportions, or The quantities of the constituents of each compound exhibit a fixed relation to one another and to the quantity of the compound formed from them* (see 57).

III. **The law of multiple proportions.** *When two elements form more than one compound, the quantities of one element which combine with a given quantity of the second exhibit a simple multiple relation* (see 59).

Some other important laws must now be briefly referred to, e.g. 'The Law of Reciprocal Proportions' and the 'Principle of the Conservation of Energy.' The latter might have been discussed conveniently immediately after 'The Principle of the Conservation of Mass,' and therefore it will be best to consider this law next. But

before we do so it is necessary to explain the use of the term *energy*, which must occasionally be employed in the following pages.

Energy may be defined as *the power to do work*, and the available energy of a body, or of a system of bodies, may be measured by the amount of work they can do. For example, a gram of hydrogen in combining with 8 grams of oxygen gives out about 34,000 units of heat, whilst the same amount of hydrogen in combining with 35.2 grams of chlorine gives out only 22,000 units of heat. Now if these two quantities of heat were employed to do work, to run a locomotive engine, for example, or lift a weight, the amount of work done, if all waste were avoided, would be in the ratio

$$34 : 22.$$

Hence the energies of the two systems are in this same ratio, provided that all their energy was obtained in the form of heat in each case.

81. 'The principle of the conservation of energy.'

It will have been noticed that in many changes, as in burning, heat is evolved, but that in others, as in the decomposition of mercury oxide, it has to be supplied from an external source. and it has long been recognized that all chemical change is accompanied either by an evolution or by an absorption of 'energy' as heat or in some other form. It may further be said that as a rule combination is accompanied by an evolution of energy and that decomposition involves its absorption*.

From various considerations, which must be sought in works on physics, it is held that 'the total energy of any material system is a quantity which can neither be increased nor diminished by any action between the parts of the system, though it may be transformed into any of the forms which energy is able to assume.'

According to this statement we must suppose that when energy is spent, for example, in effecting the decomposition of x grams of carbon dioxide into carbon and oxygen it is not destroyed, but remains

* Owing to the physical changes which frequently accompany chemical change, there are various *apparent* exceptions to this statement. For example, if a solid A combines with a gas B to form a gas AB , it is possible that energy may be absorbed. Because though the combining of A and B is accompanied by a definite evolution of energy, the volatilizing of A would absorb a definite quantity of energy, and if the latter quantity should be greater than the former their sum would be a negative quantity.

stored up, as it were, in the carbon and oxygen, and ready to reappear undiminished in quantity (usually in the form of heat) when they recombine.

A fuller treatment of the subject of heat of combination will be found in 321.

82. The law of reciprocal proportions. It can be shown by analysis that about 35.2 parts of chlorine and 126 parts of iodine respectively unite with 1 part of hydrogen. Chlorine and iodine, however, also combine chemically, and they do so in the proportions of 35.2 of chlorine to 126 of iodine: in other words, the quantities of these elements which combine with unit quantity of hydrogen will also combine with one another. The analyses of great numbers of chemical compounds have shown that this statement concerning chlorine, iodine, and hydrogen is but one case of a general law, viz. that:—

The quantities of two or more elements which respectively combine with a given quantity of a third element are either the quantities of these elements which combine with one another, or have a simple numerical relation to those quantities.

83. Gay-Lussac's law of volumes. *When two or more gases combine they do so in volumes which exhibit simple numerical relations to one another and to the volume of the product in the gaseous state.* Thus 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of water-vapour. And 1 volume of hydrogen combines with 1 volume of chlorine (144) to form 2 volumes of hydrogen chloride.

This important law was first recognized by Gay-Lussac. As will readily be seen, it confirms the Laws of Constants and Multiples in a remarkable manner.

84. Equivalent or combining weights. We can assign to each element a number, called its *equivalent or combining weight*, which has a simple relation to the quantities of the element which will combine with corresponding quantities of the other elements. We can therefore combine the Law of Multiples and the Law of Reciprocals in the following simple statement, which may be called the *Law of Equivalents*. *The elements combine in the ratios of their combining (or equivalent) weights, or in ratios which bear a simple relation to these weights.*

85. Methods of finding the combining or equivalent weights of the elements. When we study the composition of the compounds of the chief elements, we find that hydrogen enters into combination in smaller proportions than any other element. We express this by saying that hydrogen has the smallest equivalent weight, and we adopt unit mass of hydrogen for our standard of comparison in fixing the equivalent weights of the other elements. To find the equivalent weight of any element we may analyse a compound of that element with hydrogen and take as its equivalent the amount which is associated with one part of hydrogen. For example, according to Dumas water consists of 11.14 per cent. of hydrogen and 88.86 per cent. of oxygen (see 56):—

$$\begin{array}{lcl} 11.14 \text{ of hydrogen combine with } 88.86 \text{ of oxygen,} \\ \therefore 1.0 \quad \quad \quad \text{,,} \quad \text{combines with } \frac{88.86}{11.14} = 7.98. \end{array}$$

Hence 7.98 is the equivalent weight of oxygen.

If we could find the exact composition of a compound of every element with hydrogen it would be a comparatively simple matter to calculate their equivalent weights. Unfortunately we cannot do this, and therefore indirect methods, such as those which follow, must often be resorted to.

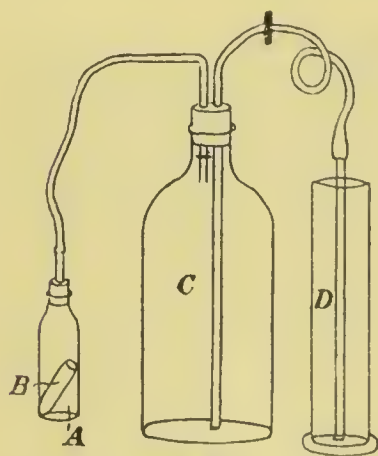


Fig. 53.

EXPERIMENT 73. To find the equivalent weight of magnesium from the hydrogen it displaces when it interacts with an acid. Place about half a gram of clean and carefully weighed magnesium turnings in a small wide-mouthed bottle *A*, together with enough water to cover them and a tube *B* containing strong hydrochloric acid. Connect *A*, as in Fig. 53, with a bottle

C, containing a litre of water. Make sure that the apparatus is airtight; pour the acid from *B* into *A*; collect the water expelled in *D*; allow *A* to cool; measure the water in *D*, and from its volume calculate the weight of the liberated hydrogen. If the water in *C* be covered with a layer of oil, soluble as well as insoluble gases may be collected.

Let us suppose 0.5 gram of magnesium were taken, and 465 c.c. of hydrogen generated.

Now 465 c.c. of hydrogen weigh $0.09 * \times \frac{465}{1000} = 0.041$ gram.

Then since

0.041 gram of hydrogen is set free by 0.5 gram of magnesium,

$$1 \quad , \quad , \quad , \quad , \quad \frac{0.5}{0.041} = 12.2 \text{ grams of magnesium}$$

From this result it appears that 12.2 grams of magnesium combine with as much chlorine as will combine with unit mass of hydrogen. Let us call this quantity of chlorine x .

Then 12.2 of magnesium and unit mass of hydrogen are each equivalent to x of chlorine.

Therefore 12.2 of magnesium and unit mass of hydrogen are equivalent to one another (Law of Reciprocals, 82).

That is to say, 12.2 is the equivalent weight of magnesium.

86. Definition of equivalent weight. From Experiment 73 the student will understand that our definition of an 'equivalent weight' may be expanded conveniently into the following statement:—

The equivalent weight of an element is that weight of the element which will combine with or replace unit quantity of hydrogen.

But just as some elements do not form compounds with hydrogen, so others will neither combine with it, nor liberate it from acids. In such cases we must study the composition of compounds of the element with other elements whose combining numbers are already known.

For example, copper does not form a suitable hydride, nor will it liberate hydrogen from an acid, as magnesium does. On the other hand, it forms a stable oxide. Now we know from 56 that the equivalent weight of oxygen is 7.9, or very nearly 8. Therefore we may ascertain how much copper combines with 8 parts of oxygen, and take this quantity to be its equivalent weight, or at least simply related to that weight.

EXPERIMENT 74. To find the equivalent weight of copper by reducing its oxide (Fig. 32). Place about two grams of dry oxide of copper ‡, carefully weighed, in a small porcelain boat in

* 1 litre of hydrogen (= 1000 c.c.) weighs nearly 0.09 gram.

‡ Cupric oxide suitable for this experiment may be made by *cautiously* igniting freshly precipitated Cu_2O in lumps made by draining and pressing the precipitate.

a piece of hard glass tube *E*, reduce it at a red heat by the action of hydrogen (Expt. 53), and weigh the copper produced. Then calculate the equivalent weight of copper as in the following example:—

I. Copper oxide and boat . . . = 20.00 grams.

Boat only = 18.42 „

Copper oxide taken = 1.58 „

II. Boat and copper = 19.68 „

Boat only = 18.42 „

Copper in 1.58 of oxide . . . = 1.26 „

Then 0.32 of oxygen is equivalent to 1.26 parts of copper

∴ 1 „ „ „ $\frac{1.26}{0.32}$ „ „

And 8 „ are „ $\frac{1.26}{0.32} \times 8 = 31.5$ parts of copper.

Therefore 31.5 is the equivalent weight of copper, or bears some simple relation to that equivalent weight. To finally ascertain the value we should have to redetermine the equivalent weight by analysing other compounds of copper. If we did this we should find our results could be arranged in two well-defined sets: one set giving 31.5 for the equivalent weight of copper, the other giving 63 (31.5×2). In such a case we usually adopt the lowest value.

EXPERIMENT 75. To determine the equivalent weight of **magnesium from the composition of its oxide.** Repeat Experiment 1, heating a carefully weighed quantity of the magnesium strongly in air until its weight becomes constant. Then from the weight of the metal taken, and that of the oxide formed, calculate how much magnesium combines with one equivalent of oxygen.

Problems. (Answers will be found on p. 513.)

1. 0.2 gram of magnesium when dissolved in acid gives 195.5 c.c. of hydrogen at 13°. Find the equivalent weight of magnesium.

2. 0.5 gram of zinc dissolved in acid gives 183 c.c. of hydrogen at 9° and 748 mm. Find the equivalent of zinc.

3. Calculate the equivalent of copper if 73.34 grams of the metal combine with oxygen to form 91.79 grams of copper oxide.

4. 0.100 gram of a metal on solution in dilute sulphuric acid gives off 84.15 c.c. of hydrogen at 0° and 760 mm. pressure. Find its equivalent,

5. One oxide of carbon contains 72.7 per cent. of oxygen, another 57.14 per cent. Show that this is in accordance with the Law of Multiple Proportions, and calculate the equivalent of carbon.

87. Some other uses of the word 'equivalent.' If any quantity a of a substance A interact with b of a substance B , then a and b may be said to be equivalent to each other.

The equivalent weight of an acid is the quantity which contains unit mass of hydrogen replaceable by metals, and the equivalent of a base is that weight of the base which neutralizes an equivalent of an acid. Again, an equivalent of a salt may be said to be the weight of the salt produced by neutralizing an equivalent of an acid or of a base.

DALTON'S ATOMIC THEORY.

The introduction of this theory into chemistry constitutes one of the most important steps in the history of the science. It is based upon the laws of combination.

The 'Law of Constant Composition' (57) was, in effect, discovered by the German chemists, Wenzel and Richter, but the doctrine that every chemical compound contains its constituents in certain fixed proportions was only finally established in the early years of this century by Proust. The 'Law of Multiples' (59) was first recognized by John Dalton (b. 1766, d. 1844) in the course of the inquiries and speculations which ultimately led him to formulate his great theory.

88. Atoms. According to the atomic theory, the matter or stuff of which things are made is not indefinitely subdivisible, but consists of a finite, though immense, number of exceedingly minute indestructible particles, which we call *atoms*. According to the theory these atoms attract one another in varying degrees, and chemical combination consists in the coming together of atoms in consequence of this attraction, which may conveniently be called 'chemical attraction.' It is further supposed that all the atoms of a given element are alike in regard to their weight and other properties, but that the atoms of any one element differ from those of every other element. Thus all atoms of hydrogen are supposed to be of equal weight and in other ways similar, and so are all atoms of oxygen, but hydrogen atoms are supposed to differ more or less from oxygen atoms in all respects, except that both possess the fundamental property of indestructibility.

If we compare the atomic theory with the laws of combination * we see that they are concordant. For example, matter made up of a finite number of indestructible and uncreatable particles would as a whole be indestructible and uncreatable. Again, if the atomic theory be true, chemical combination could only take place in accordance with the Laws of Constants and Multiples (see 80). Let us suppose, for example, that atoms of oxygen are sixteen times as heavy as atoms of hydrogen. Then since combination can only take place between definite numbers of atoms, and since these atoms have fixed weights, water cannot exhibit slight variations in its composition. A given particle of water might contain two atoms of hydrogen weighing 2, with one atom of oxygen weighing 16, or 1 part of hydrogen to every 8 parts of oxygen, but, since fractions of atoms cannot exist, it could not contain slightly different proportions, such as 8.2 parts of oxygen to 1 of hydrogen. It is conceivable, of course, that one particle of water might consist of 16 parts of oxygen with 2 of hydrogen, and another of 16 parts of the former to 1 of the latter, for one atom of oxygen, 16, might combine with one of hydrogen, but we find such differences of composition as these are accompanied by differences of property like those we have met with in the case of the two oxides of hydrogen, water and hydrogen peroxide.

89. The use of a theory. It is possible that at this stage some reader may be disposed to ask, Do chemists really believe that the atomic theory is true? The answer is, that they do not know. The important question about this, and all similar theories, is not—Do they give us true and complete pictures of the subjects they deal with, but—Has each a sufficient element of truth in it to be useful? A theory like the atomic theory is, or ought to be, a kind of tool, something to be used as long as we can do good work with its aid, but which must be discarded when it ceases to be efficient for its purpose. So long as a theory is fruitful in promoting discovery, and as long as it helps us to grasp the subject to which it relates, it may be retained and used, but we must be ever on the watch to improve it, and ready to set something better in its place on the first opportunity.

The justification for the position given to the atomic theory by chemists is this, that it has done splendid service in the past, and seems likely to be useful in the future. It should be added that, since the

* The reader must not forget that the theory was originally based on these laws.

atomic theory was first expounded by Dalton in 1808, it has undergone some modifications and expansions, and that further changes are not unlikely to become necessary as our knowledge progresses.

90. Molecules. It is thought that when a number of atoms unite to form a chemical compound, they arrange themselves in groups characteristic of that compound. For example, if a million atoms of oxygen should unite with two million atoms of hydrogen, we believe that they would not form a single mass of water containing three millions of atoms, but a million little particles of water, each containing an atom of oxygen and two atoms of hydrogen. These particles are called *molecules*.

We may gain a clear idea of the distinction between atoms and molecules by considering what would be the effect of dividing and subdividing a piece of ice or a drop of water to the utmost conceivable extent. Since particles of water are made up of two kinds of atoms, it is clear that we could not continue such a process indefinitely, but must presently reach a stage at which any further subdivision of the water would separate it into atoms of oxygen and hydrogen. At this stage we should have the smallest conceivable particles of matter which could have the properties of water; these would be its molecules. We may therefore say that *a molecule is the smallest mass of any element or compound which can be supposed to exist alone and have the properties of that element or compound.*

91. Weighing atoms and molecules (Avogadro's hypothesis). It has been calculated that many millions of molecules can be packed in so small a space as a cubic centimetre, and atoms are of course still smaller. Therefore we cannot hope to capture and weigh single molecules or atoms, but must always deal with them in large numbers.

Early in the present century an Italian man of science, Avogadro, struck by the fact that all permanent gases behave very similarly when submitted to similar changes of temperature and pressure, suggested that this mechanical resemblance might imply the existence of a corresponding similarity in the constitution of the gases, and put forward an hypothesis on the subject which may be expressed in the following words:—*Equal volumes of all true gases under equal conditions as to temperature and pressure contain equal numbers of molecules.*

If this hypothesis be true, it follows that the densities of gases (i. e. the masses of equal volumes of them) are proportional to their

respective molecular weights, and that the latter may be deduced from the former.

Let us apply this to the case of hydrogen and oxygen :—

A litre of oxygen weighs sixteen times as much as a litre of hydrogen.

But if a litre of oxygen contains n molecules, then a litre of hydrogen also contains n molecules. [Avogadro's hypothesis.]

Therefore n molecules of oxygen weigh sixteen times as much as n molecules of hydrogen.

And therefore a single molecule of oxygen weighs sixteen times as much as a single molecule of hydrogen.

But for certain reasons, which will follow, it is convenient to adopt 2 for the weight of a molecule of hydrogen*, and therefore 32 must be taken to be the molecular weight of oxygen.

Therefore, in order to find the molecular weight of a gas, or of a volatile substance, we may determine its density in terms of the density of hydrogen taken as 1, and multiply the value obtained by 2.

A simple method for finding the densities of gases has already been given (60); exact determinations are difficult to carry out, and quite beyond the powers of a beginner. The following method can be employed in the case of volatile liquids or solids :—

EXPERIMENT 76. To find the molecular weight of a volatile substance by Victor Meyer's method (Fig. 54).

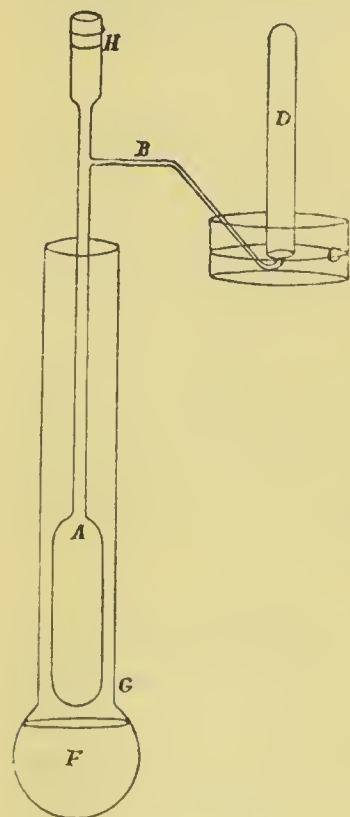


Fig. 54.

Place a little pure ether in a small stoppered bottle of known weight, and weigh the bottle and its contents. Place a Victor Meyer's vapour-density flask *A* inside a steam jacket *G* containing water at *F*, let the delivery tube *B* dip under water in *C*, and heat the water at *F* till it boils freely. When bubbles of air no longer escape from *B*, place the receiver *D* in position, remove the cork *H*, drop

* See 145.

the bottle of ether into A^* , and quickly replace H in its original position. The ether will evaporate, expelling the stopper, and its vapour will displace a corresponding volume of air from A which will pass into D . When air ceases to escape from B , measure the volume collected in D , and note its temperature and pressure in the usual manner. From the data obtained calculate the weight of an equal volume of hydrogen, and the molecular weight of ether.

For example, let 0.15 gram be the weight of the ether taken, and 47.5 c.c. the volume of the air at 13.7° and 771.6 mm., and let the tension of water-vapour at 13.7° be 11.6 mm.

Then the volume of the air under standard conditions will be (see 63, 64, 65) —

$$47.5 \times \frac{273}{273 + 13.7} \times \frac{771.6 - 11.6}{760} = 45.3 \text{ c.c.}$$

Therefore 0.15 gram of ether in the state of vapour occupies 45.3 c.c. at 0° and 760 mm.

Now since 1 c.c. of hydrogen weighs 0.00009 gram, 45.3 c.c. of hydrogen must weigh $45.3 \times 0.00009 = 0.004077$ gram. Finally, if we divide the weight of 45.3 c.c. of ether vapour by the weight of 45.3 grams of hydrogen, we get $\frac{0.15}{0.004077} = 36.8$ for the density of ether, and therefore $36.8 \times 2 = 73.6$ is its approximate molecular weight.

It need hardly be pointed out that the water in G may be replaced by liquids of higher boiling-point. Indeed, if A be made of platinum or porcelain, G may be replaced by a furnace, if it be necessary to employ a very high temperature. There are several other methods of finding vapour densities besides that described; but accounts of these must be sought in one of the larger treatises.

92. Non-volatile substances. The freezing-point, or cryoscopic, method for finding molecular weights. A very convenient method of finding the molecular weights of non-volatile substances depends upon the fact that the freezing-points of water and of some other solvents are lowered by the addition of soluble substances; and that in the case of a sufficiently dilute solution the depression produced is approximately proportional to the number of molecules of the substance present in a given mass of the solvent. Therefore, if a molecular proportion in grams of any substance is dissolved in 100 grams of water †, the depression of the freezing-point

* There should be a pad of dry glass wool to break its fall.

† Far weaker solutions are used.

is a constant K . When this constant, which is called the molecular depression of the solvent, is known for any solvent, it is only necessary to find how much of a given substance is required to produce that depression in order to know the molecular weight of the substance.

The experiment can only be made by those who possess a thermometer reading to hundredths of a degree, but the following outline of the process of finding the molecular weight of sugar will help you to understand the preceding passages.

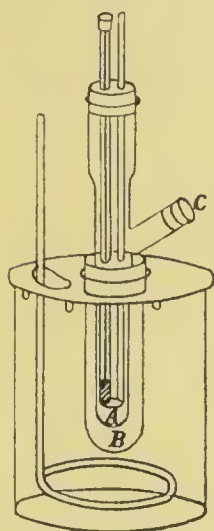


Fig. 55.

About 25 grams of water, carefully weighed in a tube A (Fig. 55), are cooled till ice begins to form. A is then wiped and placed in the jacket B , which is immersed in a freezing mixture at about -5° , till the thermometer in A falls to a temperature below the freezing of the water. The latter is then stirred vigorously, when the thermometer rises and becomes stationary at the freezing-point. A weighed amount of sugar, say half a *gram*, is now added to the water through C and dissolved, and the freezing-point of the solution is determined as before. The difference between this and the freezing-point of water gives the depression D .

Then, if P be the weight in grams of sugar dissolved in 100 grams of water, and D the observed amount of the lowering of freezing-point, $\frac{D}{P}$ gives the lowering that would be produced by 1 gram of sugar in 100 grams of water. And if M be the molecular weight of sugar, then $\frac{DM}{P}$ gives the effect of a molecular proportion of sugar in 100 of water, which is the constant K .

In the case of carbon compounds dissolved in water, $\frac{DM}{P} = 19$. Therefore, when the values of D and P are known, we can calculate the value of M .

Another method of finding molecular weights is based on the fact that non-volatile substances dissolved in volatile liquids raise the boiling-points of the latter. Neither this nor the cryoscopic method can be applied indiscriminately, for certain classes of solids, e. g. mineral acids and salts, do not behave exactly as stated above.

93. Chemical methods of fixing molecular weights. It

is often possible to fix the molecular weight of a substance from chemical considerations as in the following example:—13 parts of benzene contain 12 parts of carbon and 1 of hydrogen, and one-sixth of this hydrogen can be replaced by chlorine, 35.2 parts of chlorine taking the place of 1 part of hydrogen. Now, assuming that every molecule of benzene is similarly affected by the chlorine, we could not replace one-sixth of the hydrogen in benzene unless each molecule contained at least six atoms of hydrogen *, for atoms are indivisible.

But the atomic weight of hydrogen is taken as 1, and 6 parts of hydrogen are present in 78 parts of benzene; therefore 78 is taken to be the molecular weight of benzene.

Again, it was at one time supposed that the molecular weight of sulphuric acid might be 49. But the atomic weight of sulphur has been fixed at 32, and 49 parts of sulphuric acid contain only 16 parts of sulphur †. Now, since atoms are indivisible, a molecular proportion of sulphuric acid cannot contain less than an atomic proportion, that is, 32 parts, of sulphur. Hence 98 is the smallest value we can adopt for the molecular weight of sulphuric acid.

Often it is only possible to ascertain the approximate molecular weight of a substance by the above or similar methods. In this case a knowledge of the exact composition of the substance may help us to arrive at a more precise determination.

Let us suppose, for example, that the density of carbon dioxide had led us to adopt the number 45 for its approximate molecular weight, and that we found the substance to consist of carbon and oxygen in the proportions of 3 of carbon to 8 of oxygen exactly. Then we should adopt 44 for its molecular weight, because we know that the elements combine in the ratios of their equivalent weights, or in proportions simply related to them (84), and 44 parts would contain four equivalent proportions (see 84 and 86) of carbon, 3×4 , united with four equivalent proportions of oxygen, 8×4 .

When no sufficient information can be obtained, the molecular weight which best agrees with the simplest formula (101) of a substance may be adopted provisionally.

94. Atomic weights. Since atoms are indivisible it follows that no molecule can contain less than one atom of any constituent element. Therefore we may define the atomic weight of an element

* Or some multiple of six atoms.

† All these quantities are in terms of the weight of an atom of hydrogen.

as the smallest weight of the element which has ever been found in a molecular proportion of the element or of any compound containing it.

The true atomic weight of the element might conceivably be a sub-multiple of this quantity, but it could not have a greater value.

The student will now understand why we began the discussion of this subject by describing some simple methods of fixing molecular weights. It was desirable that he should understand a few of the chief methods of weighing molecules before proceeding to study atomic weights, because the latter quantities can best be defined with reference to the former.

It has been found that hydrogen has the lightest atom, and therefore it is convenient to adopt 1 for the atomic weight of hydrogen, and to express the weights of other atoms in terms of this quantity. Thus the atomic weights are the relative weights of the atoms of the various elements expressed in terms of the weight of an atom of hydrogen*, just as molecular weights are the relative weights of molecules in terms of the same standard.

The ideal method for finding the atomic weight of an element would be to prepare all the compounds of that element, and to find the composition of every one of those compounds and also their molecular weights. Then the smallest quantity of the element found in a molecular proportion of any compound, or of the element itself, might be adopted as its atomic weight. In practice, however, it is never possible to carry out such an ideal research, and chemists must be content to employ less perfect methods.

95. Specific heat† and atomic weight. It is found that very different quantities of heat are required to raise the temperatures of equal weights of water, platinum, lead, silver, zinc, &c., through an equal number of degrees, say, for example, from 0° to 100° .

Thus the amount of heat required to raise a kilogram of water from 0° to 100° is thirty-one times as great as that required to raise the temperature of a kilogram of platinum to the same extent.

The amount of heat required to raise unit mass of a substance through 1° is known as its *specific heat*.

Equal masses of these substances are therefore said to possess

* i. e. of the smallest quantity of hydrogen found in any molecule containing it.

† A work on practical physics should be consulted in order to learn how specific heats are measured.

different specific heats. As the specific heat of water is greater than that of almost all other substances, it is usual to state specific heats in terms of the amount of heat required to warm 1 gram of water from 0° to 1° . Thus the specific heat of platinum is $\frac{1}{31}$ or 0.032.

In the year 1819 Dulong and Petit compared the specific heats and atomic weights of a number of solid elements. They observed that the former exhibited an inverse relation to the latter, and concluded that the capacities for heat of the atoms of the elements examined were equal.

Subsequent investigations have not entirely confirmed this conclusion, but it remains true that in a majority of the cases hitherto studied the product of the specific heat and atomic weight of a metallic element in the solid state approximates to the constant 6.4, as shown in the following illustrative table:—

TABLE OF SPECIFIC HEATS OF SOME ELEMENTS.

<i>Name.</i>	<i>Specific Heat.</i>	<i>Atomic Weight (approximate).</i>	<i>Atomic Heat = Specific Heat × Atomic Weight.</i>
Lithium	0.94	7.0	6.6
Sodium	0.293	23.0	6.7
Magnesium . . .	0.245	24.0	5.9
Aluminium . . .	0.225 (?)	27.0	6.1
Potassium . . .	0.166	39.0	6.5
Iron	0.112	55.9	6.3
Copper	0.093	63.4	6.0
Zinc	0.093	64.9	6.1
Silver	0.056	107.6	6.0
Tin	0.055	117.8	6.5
Platinum	0.032	195	6.3
Iodine	0.054	127.5	6.8
Arsenic, crystalline	0.082	74.9	6.1
Sulphur, rhombic .	0.163	32	5.2
“ “	0.178	32	5.7
			mean 5.4

The most striking exceptions to Dulong and Petit's rule occur in the cases of the non-metals, carbon, boron, and silicon; the atomic heats of

these elements at ordinary temperatures being respectively about 2.2, 2.6, and 4.7 *. At higher temperatures, however, they approach the normal value much more closely, as shown below :—

Atomic heat of carbon at 985° 5.5.

„ „ boron „ 1000° 5.0.

„ „ silicon „ 232° 5.7.

96. Application of Dulong and Petit's Law. It will readily be understood that Dulong and Petit's Law affords us a method of fixing atomic weights, which is especially useful in the case of those elements which form but few volatile compounds.

The following example will explain how the rule may be applied :—

The specific heat of aluminium is 0.225.

Now atomic weight $\times$ specific heat = 6.4 ;

$\therefore \frac{6.4}{.225}$ gives us the approximate atomic weight of aluminium, viz. 28.4.

But the equivalent weight of aluminium is 8.97. Therefore its atomic weight is $8.97 \times n$. And the value of n which agrees most closely with the approximate atomic weight found above is 3, which leads to 26.9 for the true atomic weight of aluminium.

97. Relation between the values of equivalent weights and atomic weights. If any atom having the weight A unite with hydrogen, then it must unite with one or more whole atoms of hydrogen, because atoms are indivisible.

Let n be the number of atoms of hydrogen with which A can unite.

Then $\frac{A}{n}$ parts of the element will unite with one atom of hydrogen.

But the *atomic weight* and *equivalent weight* of hydrogen are both expressed by the same number, viz. 1.

Therefore $\frac{A}{n}$ is the *equivalent weight* of the element, that is, the amount of it which will combine with one part of hydrogen.

And since n is a whole number it follows that the atomic weight A must be a simple multiple of the equivalent weight $\frac{A}{n}$.

We have just seen how advantage is taken of this fact when we seek

* The exact values depend on the forms in which the elements are taken. Thus for diamond the value is 1.8, for graphite 2.1 to 2.4.

the aid of Dulong and Petit's Law in determining an atomic weight. It may be similarly applied in other cases.

Let us suppose, for example, that we have analysed a number of compounds containing oxygen, and have found the smallest amount of oxygen present in a molecular proportion of any one of them to be 16. Also that a very exact analysis of water has shown us that the equivalent weight of oxygen is 7.93. Then we must adopt the value 15.86 (7.93×2) for the atomic weight of oxygen rather than 16.

This will explain why chemists take so much pains to learn the exact equivalent weights of the elements. It is because a knowledge of the equivalent weight of any element helps us to determine its atomic weight.

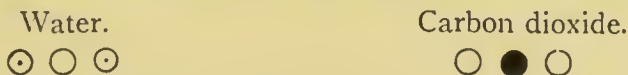
The student may now attempt to solve problems 32 to 41—omitting 35 and 36—on p. 501.

98. Notation. When Dalton first expounded his atomic theory, he invented a method of representing atoms and their combinations by symbols and formulæ, which aided him materially in conveying his ideas to others and which, in a modified form, is still used.

SOME EXAMPLES OF DALTON'S SYMBOLS.

An atom of Oxygen . .	○	An atom of Carbon . .	●
„ „ Hydrogen . .	◐	„ „ Iron . . .	Ⓘ
„ „ Nitrogen . .	Ⓛ	„ „ Tin . . .	Ⓣ

In order to represent compounds, Dalton grouped together the symbols of their constituent elements, making such picture formulæ as the following, which represent water and carbon dioxide respectively:—



But though these symbols helped Dalton to explain his ideas the system was too cumbrous to be long retained, and, at the suggestion of Berzelius, Dalton's circles and picture formulæ were soon replaced by the simpler system described below.

99. Chemical symbols and formulæ. A *symbol* represents an atom of an element. Thus H stands for one atom of hydrogen weighing 1; O for one atom of oxygen weighing 16; C for an atom of carbon, and so on. A list of these symbols was given on page 47.

A molecule is represented by a collection of symbols which is called

a *formula*. Thus O_2 is the formula of a molecule of oxygen containing two atoms ; H_2 represents a molecule of hydrogen which also contains two atoms ; Hg represents a molecule of mercury consisting of one atom ; and P_4 a molecule of phosphorus containing four atoms. The molecules of the volatile elements do not usually consist of single atoms, as in the case of mercury, but most frequently of two or more, as indicated by the numeral written below the symbol in each case.

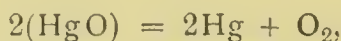
The formula of a compound is constructed by writing, side by side, the symbols of its constituent elements, the number of atoms of each element present in a molecule being indicated by numerals as before.

Thus a molecule of water contains two atoms of hydrogen and one of oxygen, and its formula is H_2O .

A molecule of ammonia contains one atom of nitrogen with three of hydrogen. Its formula is NH_3 .

In order to express 2, 3 or x molecules of an element or compound we place a numeral before its formula. Thus $2H_2O$, $3H_2O$, and xH_2O mean two, three and x molecules of water respectively.

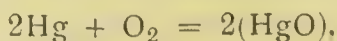
100. Chemical equations. Aided by one or two symbols borrowed from algebra, we can express chemical changes by means of the above symbols and formulæ in the very convenient form of *chemical equations*. In these equations the $+$ sign is used to express the adding of one substance to another, whilst the $=$ sign, besides indicating equality, as in algebra, is used where the word 'produce' would be appropriate. Thus we express the effect of heating oxide of mercury by writing :—



which means that two molecules of mercury oxide ($2HgO$) produce two molecules of mercury ($2Hg$), containing one atom of mercury in each, and a molecule of oxygen (O_2), containing two atoms of oxygen.

Whenever you find the $+$ sign between two formulæ, as in the above equation, you are to understand that the substances whose formulæ are thus divided are *not* combined.

Combination (42 and 43) is expressed by equations in which the formulæ of the substances which combine stand on the right. Thus :—



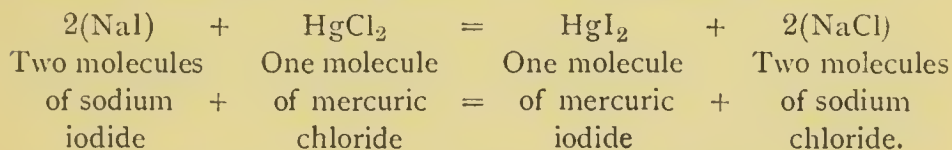
tells us that two molecules of mercury ($2Hg$), each containing one atom of mercury, combine with one molecule of oxygen (O_2), containing two atoms of oxygen, and produce two molecules of oxide of mercury ($2HgO$).

Substitution (45). The equation which expresses the action of zinc on hydrochloric acid, affords another simple illustration of the use of symbols, and will help you to grasp the nature of the change far better than words :—

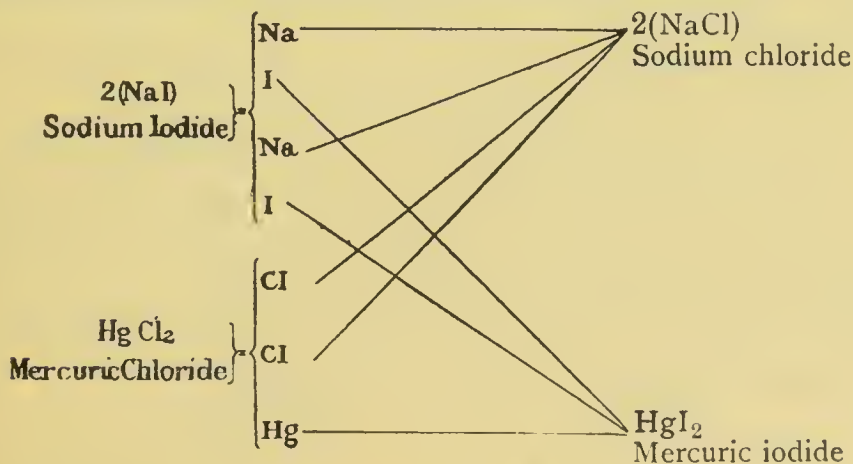


From this equation we see that an atom of zinc (Zn) replaces the hydrogen in two molecules of hydrochloric acid (2HCl), setting free a molecule of hydrogen (H₂), and forming a molecule of zinc chloride (ZnCl₂), which contains one atom of zinc united with two atoms of chlorine.

Double decomposition (46). The behaviour of a soluble iodide with mercuric chloride (Expt. 43) can be equally well expressed by means of this chemical algebra. The formula of sodium iodide is NaI ; that of mercuric chloride, HgCl₂. When these two salts are mixed their metals change places, so that sodium chloride (NaCl) and mercuric iodide (HgI₂) are produced. This is expressed as follows :—



Beginners will find it helpful to trace the transpositions of the atoms in this reaction by means of the following diagram, in which the formulæ of the compounds taken are placed on the right, and those of the products of the rearrangement of their atoms on the left.



The brackets in such an expression as 2(NaI) are usually omitted, but they help the beginner to grasp the fact that the figure 2 in this

position does not mean two atoms of sodium united with one of iodine, but two molecules of sodium iodide, each containing one atom of sodium and one atom of iodine.

101. How formulæ are fixed. Let us suppose that we want to find the formula of the gas *ethane*, that its percentage composition has been found to be :—

Carbon	= 80.0 parts
Hydrogen	= 20.0 „
	100.0 „

and that its density is 15.

Then since the atomic weight of carbon is 12 and that of hydrogen 1, we can easily find how many atomic proportions of each are present in 100 parts of ethane :—

Carbon	= $80 \div 12 = 6.6$
Hydrogen	= $20 \div 1 = 20$

Now

$$20 : 6.6 :: 3 : 1.$$

Therefore there are three atomic proportions of hydrogen to one atomic proportion of carbon in ethane.

Hence its formula is CH_3 or some multiple of CH_3 .

Now the density of ethane is 15.

Therefore its molecular weight is 30 (91).

If the formula of ethane be CH_3 , its molecular weight must be 15, for the weight of a molecule must be equal to the sum of the weights of its constituent atoms.

But if the formula of ethane be C_2H_6 its molecular weight must be 30, for $12 \times 2 + 1 \times 6 = 30$. Hence its formula is C_2H_6 .

It will be understood that since a formula represents a molecule, it can only be correctly ascertained when data are available for fixing the molecular weight of the substance to be represented. A formula such as CH_3 is sometimes called the *simplest formula* of a substance to distinguish it from the true or molecular formula.

Problems. (For answers see Answers 21, 30 and 22 on pp. 513, 514.)

1. A compound of iron and oxygen has the composition—

Iron	= 70.0
Oxygen	= 30.0
	100.0

Find its simplest formula.

2: Sugar has been found to contain—

Carbon	= 42.11
Hydrogen	= 6.43
Oxygen	= 51.46
	100.00

Find its simplest formula.

3. A volatile acid is found to contain—

Carbon	= 40.0
Hydrogen	= 6.6
Oxygen	= 53.4
	100.0

Given that its vapour density is 30, find its molecular formula.

102. Chemical names—Nomenclature. If the table of the elements on p. 47 be inspected, it will be found that very many of their names end in *-um*. These are *metals*; the rest, with some exceptions, are not metals, and are called *non-metals*. To distinguish the metals more exactly their Latin names are usually added to their more familiar names, when the latter do not carry the distinctive termination.

The names of compounds of two elements are usually built up from those of their components, but they end in *-ide*. When one of the elements is a metal and the other a non-metal, the change of termination is made in the name of the non-metal.

Thus we have :—

NaCl	Sodium chloride
CaO	Calcium oxide
PbS	Lead sulphide
H ₂ O	Hydrogen oxide (water).

When two elements unite in more than one proportion, a system of numerical prefixes is employed. Thus in the case of the two oxides of hydrogen we have :—

Hydrogen monoxide	H ₂ O
Hydrogen dioxide	H ₂ O ₂ .

Again we have :—

Phosphorus trichloride	PCl ₃
Phosphorus pentachloride	PCl ₅ .

When the molecular formula of a substance has not been definitely fixed, or when there are objections to the use of numerical prefixes, the termination *-ic* and *-ous* may be used, as in the following examples :

Ferrous chloride	FeCl_2
Ferric chloride	Fe_2Cl_6 or FeCl_3
Ferrous oxide	FeO
Ferric oxide	Fe_2O_3 .

Sometimes it is convenient to combine the two systems. Thus we have :—

Nitrogen monoxide (nitrous oxide)	N_2O
Nitric oxide	NO
Nitrogen trioxide	N_2O_3
Nitrogen tetroxide (nitric peroxide)	N_2O_4
Nitrogen pentoxide	N_2O_5 . (N_4O_{10} ?)

The prefixes *proto-* and *per-* may also be met with in the older works on chemistry.

Thus FeO has been called iron protoxide as well as iron monoxide, or ferrous oxide. And Fe_2O_3 , iron rust, or ferric oxide, has been called iron peroxide, and also sesquioxide of iron.

More complex substances are distinguished by somewhat similar devices. For example, the names of two of the chief acids containing sulphur are :—

Sulphurous acid or Hydrogen sulphite .	H_2SO_3
Sulphuric acid or Hydrogen sulphate .	H_2SO_4 .

And similarly we have :—

Phosphorous acid or Hydrogen phosphite	H_3PO_3
Phosphoric acid or Hydrogen phosphate .	H_3PO_4 .

The salts of these acids have names in which the terminations *-ic* and *-ous* are respectively changed into *-ate* and *-ite*. Thus sulphuric acid (H_2SO_4) forms copper sulphate (CuSO_4), and sodium sulphate (Na_2SO_4); and sulphurous acid (H_2SO_3) forms sodium sulphite (Na_2SO_3), and copper sulphite (CuSO_3).

Hydroxides. Substances which may be supposed to be derived from water (H_2O) by the replacement of half its hydrogen by a metal are termed *hydroxides*. Thus NaHO is sodium hydroxide, and CaH_2O_2 or $\text{Ca}(\text{HO})_2$ is calcium hydroxide. The term *hydrate* was formerly applied to hydroxides, and this use of the word still survives,

NaHO, for example, being often called sodium hydrate. The term hydrate should, however, be reserved for such compounds as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which is said to be *hydrated*, whilst common salt (NaCl), which does not contain the elements of water, is described as anhydrous.

The student will find that the same substance is often known by several names. For example the names soda, caustic soda, sodium hydrate, and sodium hydroxide are all applied to the compound which has the formula NaHO. This is apt to be exceedingly confusing to beginners, but it is almost inevitable that it should occur in the case of a growing science. From the point of view of the teacher and student it would be a great advantage if we could adhere to a given system of names. But even a beginner ought at the end of his course to be able to read the easier parts of the literature of his subject, and as no uniform system of nomenclature has been used by writers on chemistry, it is important that every student should acquaint himself, as far as possible, with the various names in common use.

Further details on the subject of nomenclature will be added, as they are required, in the subsequent pages.

103. The use of symbols and formulæ in chemical calculations. Since the quantities of substances which take part in chemical changes exhibit definite relations, we can calculate what amount of any element or compound we shall want to effect a given purpose. For example, since we know that 100 parts of water contain 11.11 parts of hydrogen, it is easy to calculate how much hydrogen will be required to produce 20 parts of water. In such calculations symbols and formulæ play an important part, as may be learnt by going through the following examples, and afterwards solving the exercises given in Section I, p. 493.

1. To find the molecular weight of hydrochloric acid, from its formula.

Add together the weights corresponding to the symbols in the formula HCl.

Atomic weight of H		1
„ „ Cl		35.5 *
Molecular weight		36.5

* The true value is 35.2, but approximate values may often be substituted for the exact values when one works out a problem for the sake of practice.

2. To find the molecular weight of alum from the formula $K_2SO_4, Al_2(SO_4)_3, 24H_2O$.

$$\begin{array}{rcl}
 K_2 & = & 39 \times 2 = 78 \\
 Al_2 & = & 27 \times 2 = 54 \\
 S_4 & = & 32 \times 4 = 128 \\
 O_{16} & = & 16 \times 16 = 256 \\
 24H_2O & = & 18 \times 24 = 432 \\
 \hline
 \text{Molecular weight} & . & . \quad 948
 \end{array}$$

3. To find the percentage composition of a substance when its formula is known.

Let the substance in question be mercuric oxide (HgO). Then the question before us is:—How many parts of mercury and how many of oxygen are there in 100 parts of mercuric oxide?

Find the sum of the weights of the atoms present in a molecule of mercuric oxide.

$$\begin{array}{rcl}
 Hg & . & . & . & . & . & . & . & 200 \\
 O & . & . & . & . & . & . & . & 16 \\
 & & & & & & & & \hline
 & & & & & & & & 216
 \end{array}$$

216 parts of mercuric oxide contain 200 parts of mercury,

$\therefore$ 1 part „ „ contains $\frac{200}{216}$ „ „

and 100 parts „ „ contain $\frac{200}{216} \times 100 = 92.6$ of mercury.

Again:

216 parts of mercuric oxide contain 16 parts of oxygen,

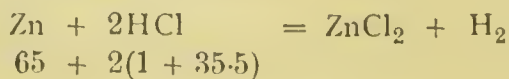
$\therefore$ 1 part „ „ contains $\frac{16}{216}$ „ „

and 100 parts „ „ contain $\frac{16}{216} \times 100 = 7.4$ of oxygen.

We might also subtract 92.6 from 100 to find the amount of oxygen.

4. To find how many grams of zinc can be dissolved in a solution containing 100 grams of hydrochloric acid (HCl).

Write the equation for the change, with the weights of the zinc and acid under their formulæ. Thus:—

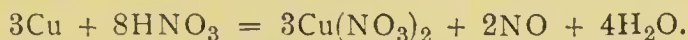


The equation shows us that :—

73 grams of acid dissolve 65 grams of zinc.
 $\therefore$ 1 gram „ dissolves $\frac{65}{73}$ „ „
 and 100 grams „ dissolve $\frac{65}{73} \times 100 = 89$ grams of zinc.

5. How much nitre (KNO_3) will be required to produce sufficient nitric acid (HNO_3) to dissolve 50 grams of copper?

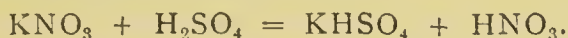
The action between copper and nitric acid may be represented by the following equation :—



From this we learn that three atomic proportions of copper, or 63×3 grams, require eight molecular proportions of nitric acid.

We must therefore take as much nitre as will produce eight molecular proportions (8HNO_3) of nitric acid, taken in grams.

Now one molecular proportion of nitre (KNO_3) will give one molecular proportion of nitric acid (HNO_3):—



Therefore eight molecular proportions, 8KNO_3 or $8(39.1 + 14 + 48)$, = 808.8 grams, of nitre are required to dissolve 189 grams of copper :—

189 grams of copper require 808.8 grams of nitre,

$\therefore$ 1 gram „ requires $\frac{808.8}{189}$ „ „

and 50 grams „ require $\frac{808.8}{189} \times 50 = 214$ grams of nitre.

6. To calculate the density of a gas when its formula is known.

Let us suppose we want to calculate the density of nitrous oxide (N_2O). Its required molecular weight is $(14 \times 2) + 16 = 44$.

Therefore its density is $\frac{44}{2} = 22^*$.

We often want to know the volumes occupied by the gaseous products of reactions, or to calculate the volume occupied by a given mass of a gaseous substance. Now it has been found by experiments that the weight in grams of 22.24 litres of any true gas, at 0° and

* See 91. It must not be forgotten that in practice the density must be found by experiment before the formula can be fixed.

760 mm., is expressed by nearly the same figures as its molecular weight. Thus the molecular weight of carbon dioxide (CO_2) is 44, and 22.24 litres of carbon dioxide under normal conditions weigh 44 grams. Again, the molecular weight of oxygen (O_2) is 32, and 22.24 litres of oxygen at 0° and 760 mm. weigh 32 grams.

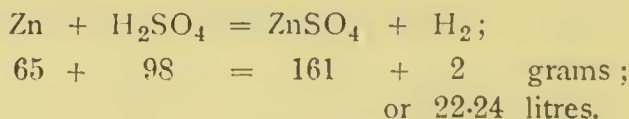
7. To find the volume occupied by 10 grams of nitrous oxide (N_2O) at 0° and 760 mm.

The molecular weight of nitrous oxide (N_2O) was found above to be 44. It follows that :—

$$\begin{aligned} & 44 \text{ grams of } \text{N}_2\text{O} \text{ occupy } 22.24 \text{ litres,} \\ \therefore 1 \text{ gram } & \text{,, occupies } \frac{22.24}{44} \text{,,} \\ \text{and 10 grams } & \text{,, occupy } \frac{22.24}{44} \times 10 = 5.05 \text{ litres.} \end{aligned}$$

8. To calculate the volume of hydrogen evolved when 100 grams of zinc are dissolved in sulphuric acid. (See also pp. 63 and 64.)

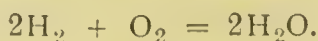
From what has been said it will be seen that we can write an equation so as to show the weights and volumes of the substances concerned :—



From this we see that :—

$$\begin{aligned} & 65 \text{ grams of zinc will set free } 22.24 \text{ litres of hydrogen,} \\ \therefore 1 \text{ gram } & \text{,, } \text{,, } \frac{22.24}{65} \text{,, } \text{,,} \\ \text{and 100 grams } & \text{,, } \text{,, } \frac{22.24}{65} \times 100 = 34.2 \text{ litres of} \\ & \text{hydrogen.} \end{aligned}$$

9. If no considerations concerning mass occur in a problem the calculation is more simple. For example, to find what volume of hydrogen will combine with 27 c.c. of oxygen we have :—

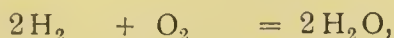


From which we see that two molecular proportions of hydrogen (2H_2) take one molecular proportion of oxygen (O_2).

But molecular proportions of gases occupy equal volumes (see Avogadro's hypothesis).

Therefore 2 volumes of hydrogen combine with 1 volume of oxygen.
And 27 volumes of oxygen require 54 volumes of hydrogen.

Or again:—



2 volumes of oxygen require 4 volumes of hydrogen,

$\therefore$ 1 volume „ requires $\frac{4}{2}$ „ „

and 27 volumes „ require $\frac{4}{2} \times 27 = 54$ volumes of hydrogen.

The student should work through as many of the problems in Section I at the end of the book as time permits. Afterwards he should work out those in Section II, but he should do the latter gradually, a few at a time, and concurrently with other work.

As soon as possible after working through the problems in Section I the student should work out the quantitative exercises given in 115, 116, in the laboratory. These will afford a far better training in practical work than merely making a few salts, &c., in a haphazard way, and at the same time will give a reality to the student's ideas about symbols and formulæ which they would not acquire from the mere working out of numerical examples on paper.

104. Valency. If we compare the formulæ of a few simple compounds, we at once perceive that all atoms do not possess equal powers of combining. For instance:—

Hydrogen chloride has the formula HCl .

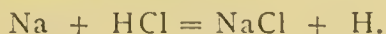
Hydrogen oxide has the formula H_2O .

Hydrogen nitride (ammonia) has the formula NH_3 .

Hydrogen carbide (marsh gas) has the formula CH_4 .

From this table we see that whilst an atom of chlorine only combines with one atom of hydrogen, one of oxygen can combine with two such atoms, one of nitrogen with three, and one of carbon with no less than four.

Again, if an atomic proportion of sodium were dissolved in dilute hydrochloric acid, an atomic proportion of hydrogen would be liberated, as indicated by the following equation:—



But if an atomic proportion of zinc were substituted for one of sodium,

twice as much hydrogen would be set free, from which it appears that the combining power, or valency, of an atom of zinc must be twice as great as that of an atom of sodium.

The *valency* of an element may be indicated conveniently by dashes or small Roman numerals placed after its symbol as in the following examples :—

Univalent elements.	.	.	.	.	H' Na' Cl'
Divalent	„	.	.	.	O'' Zn''
Trivalent	„	.	.	.	N'''
Quadrivalent	„	.	.	.	Civ S ^{iv}
Quinivalent	„	.	.	.	N ^v P ^v
Sexvalent	„	.	.	.	S ^{vi}

The valency of an atom can be most simply measured by ascertaining how many atoms of hydrogen it will combine with or replace, and atoms are classified as *univalent*, *divalent*, *trivalent*, &c. Those which combine with, or replace, one atom of hydrogen are said to be univalent, those which combine with two atoms of hydrogen divalent, and so on. In order to learn the valency of an element which does not combine with hydrogen we must study its compounds with other elements of known valency.

For example, one atomic proportion of sodium combines with one atomic proportion of chlorine to form a molecular proportion of salt.

But chlorine is univalent.

Therefore we conclude that sodium also is univalent.

Again, an atomic proportion of calcium unites with two atomic proportions of univalent chlorine to form a molecular proportion of calcium chloride. Therefore calcium is considered to be divalent.

For the present we may say that *the (maximum) valency of an atom is to be measured by the maximum number of univalent atoms with which it can combine to form a molecule, or by the number of univalent atoms which it can displace.* In attempting to fix the valency of an atom it is desirable to take into consideration only those of its compounds whose molecular weights are known.

Valency may vary. Every atom has a maximum valency, but it does not follow that it always exerts its maximum valency. For example, nitrogen atoms are trivalent in ammonia (NH₃), but may possibly be quinivalent in ammonium chloride (NH₄Cl). The valency exerted by a carbon atom in the monoxide (CO) may not be the same as in the dioxide (CO₂). Atoms of phosphorus are trivalent

in the molecule PCl_3 , but would seem to be quinquivalent in PF_5 . In such cases as the above, the effective valency of the atom whose valency varies can usually be expressed in every case either by even numbers alone or by odd numbers. Thus carbon is observed to be divalent and quadrivalent in its two oxides, and phosphorus to be trivalent and quinquivalent.

The valency of an atom is to some extent influenced by such conditions as temperature. If ammonia (NH_3) and hydrogen chloride (HCl) be brought together in the cold they combine, forming a solid salt to which the formula NH_4Cl is usually given, but if this salt be heated in a dry tube it is resolved into a mixture of ammonia (NH_3) and hydrogen chloride (HCl). Similarly, the highest chloride of phosphorus (PCl_5) is a solid which seems to exist in the gaseous state only under special conditions (see 254).

Another remarkable fact, in connexion with the theory of valency, is the tendency of certain salts to unite with water, or with one another, forming such compounds as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (50 and 539), and double salts like the alums (431). It has been suggested that in some of these compounds the molecules may be held together by an attraction peculiar to whole molecules, but it seems likely that the difficulty we find in accounting for the existence of such compounds is rather due to a defect in the theory, than to the existence of two kinds of chemical attraction. Therefore the definition of valency given on a previous page must not be accepted as final.

105. Compound radicles. If the student performs Experiments 5 and 7 described in 219 he will find that a solution of ammonia gas (NH_3) is remarkably like a solution of potash in many of its properties, and that when neutralized with acids it yields a series of salts which present a marked resemblance in solubility and crystalline form to the corresponding salts of potassium. Now a marked resemblance of this kind is usually supposed to indicate similarity of chemical constitution. Potash is formed when an atom of potassium replaces half the hydrogen in a molecule of water (H_2O), it is therefore represented by the formula KHO . How, then, can a solution produced by the combining of a molecule of ammonia (NH_3) with one of water (H_2O) be so similar to potash and the other alkaline hydroxide (NaHO)? The resemblance may be accounted for by supposing that solution of ammonia contains a compound $(\text{NH}_4)\text{HO}$, in which the group of atoms (NH_4) replaces the atom of potassium in

a molecule of potash (KHO), and that this group, which is called *ammonium*, persists when a solution of ammonia is neutralized, so that a series of compounds is formed in which the group NH_4 plays a similar part to that of an atom of potassium in the compounds of that metal, as suggested by the following formulæ:—

Potassium	hydroxide	.	.	.	.	KHO
„	chloride	.	.	.	.	KCl
„	sulphate	.	.	.	.	K_2SO_4
„	platino-chloride	.	.	.	.	$2\text{KCl}, \text{PtCl}_4$
„	carbonate	.	.	.	.	K_2CO_3
Ammonium	hydroxide	.	.	.	.	$(\text{NH}_4)\text{HO}$
„	chloride	.	.	.	.	$(\text{NH}_4)\text{Cl}$
„	sulphate	.	.	.	.	$(\text{NH}_4)_2\text{SO}_4$
„	platino-chloride	.	.	.	.	$2(\text{NH}_4)\text{Cl}, \text{PtCl}_4$
„	carbonate	.	.	.	.	$(\text{NH}_4)_2\text{CO}_3$

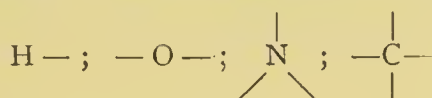
Hypothetical groups of atoms such as ammonium (NH_4) are called *compound radicles*. Many such radicles have been recognized by chemists, and they may be defined as groups of atoms which occur in the molecules of more than one compound, and can pass unchanged from one molecule to another.

The student will meet with many compound radicles, but his attention may now be directed to the group (HO), called *hydroxyl*, which occurs in ammonium hydroxide (NH_4HO), in potassium hydroxide (KHO), in sodium hydroxide (NaHO), and in many other compounds; also to *cyanogen* (CN), which occurs in the cyanides; to SO_4 , which is met with in the sulphates; to the CO_3 of carbonates, and the NO_3 of nitrates. It is not possible for the student to verify, experimentally, the existence of all these radicles for himself, but when he finds that a given group of atoms frequently appears in the formulæ of a series of allied compounds, and that this group plays a part like that of an atom in the reactions of these compounds, he may conclude that the group constitutes a compound radicle.

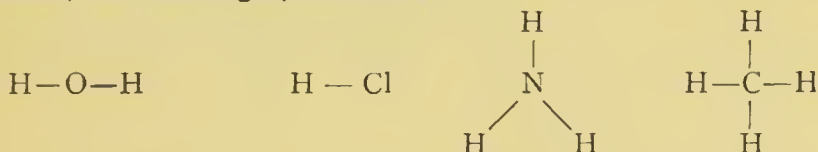
106. The valency of a compound radicle. It will be found that compound radicles exhibit a more or less definite valency like the simple radicles or atoms. For example, the group NH_4 , which combines with one atom of chlorine, and replaces one atom of potassium, is *univalent*, whilst the group SO_4 , which combines with two atoms of hydrogen to form a molecule of sulphuric acid (H_2SO_4), is considered to be divalent.

It is evident that the valency of a compound radicle is likely to depend on the state of saturation of its constituent atoms. We should expect hydroxyl ($\text{H}^{\text{I}}\text{O}^{\text{II}}$), which consists of a divalent atom united to a univalent atom, to be univalent, and carbonyl ($\text{C}^{\text{IV}}\text{O}^{\text{II}}$), in which a quadrivalent atom is united with a divalent atom, to be divalent, and to form such compounds as the dioxide CO_2 and the oxychloride COCl_2 .

107. Graphic formulæ. To indicate the supposed relations of the atoms to one another in the molecules in which they exist, their symbols are sometimes written with lines or dashes, called *bonds*, which correspond to their respective valencies, and remind us of the number of univalent atoms with which any given atom can be associated at one time. Thus we might write



In order to express compounds, these *graphic* symbols are placed so that the lines form *bonds* between the combining elements. Thus we may write the graphic formulæ of water, hydrogen chloride, ammonia, and marsh gas, as follows :—



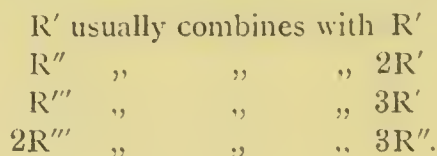
These formulæ are often useful, but it must not be supposed that they indicate the actual arrangement of the atoms in the molecules; they merely indicate in a simple and clear manner the number of units of valency possessed by each atom, and suggest how they may be disposed of in each case.

108. Writing chemical formulæ. Apart from its theoretical interest, the classification of the elements according to their valencies is very helpful, as it provides us with a means of avoiding mistakes in writing chemical formulæ, and saves us the labour of learning great numbers of formulæ by heart. The following table contains a few of the chief simple and compound radicles, classified according to their habit of combining :—

THE VALENCIES OF SOME COMMON ELEMENTS AND
SALT RADICLES.

<i>Univalent (R').</i>		<i>Bivalent (R'').</i>		<i>Trivalent (R''').</i>		<i>Quadri- valent.</i>		<i>Sex- valent.</i>
F	H	O	Ca	PO ₄ in phos }	Bi	C	Pt	S
Cl	K	S	Mg	phates }	Sb	Si	Sn	
Br	Na	SO ₄ in sul- }	Zn	AsO ₄ in arsen- }	As			
I	NH ₄	phates }	Hg (ic)	B	Al			
CN	Ag	SO ₃ in sul- }	Cu (ic)		Cr			
HO		phites }	Pb		Fe(ic)			
NO ₃ in ni- }		CO ₃ in car- }	Fe (ous)					
trates }		bonates }	Hg ₂ (ous)					
ClO ₃ in chlor- }			Cu ₂ (ous)					
ates }								
ClO in hypo- }								
chlorites }								

In writing formulæ the student must remember that—



For example, the formula of potassium chloride is $K'Cl'$, but we write for potassium sulphide K'_2S'' . In like manner, calcium oxide is written $Ca''O''$, and calcium chloride $Ca''Cl'_2$.

The following examples will serve to further illustrate the application of the rule :—

Sodium chlorate, $Na'(ClO_3)'$.
 Silver carbonate, $Ag'_2(CO_3)''$.
 Hydrogen phosphate, $H'_3(PO_4)'''$.
 Magnesium bromide, $Mg''Br'_2$.
 Magnesium sulphide, $Mg''S''$.
 Bismuth phosphate, $Bi'''(PO_4)'''$.
 Bismuth oxide, $Bi'''_2O'''_3$.
 Aluminium chloride, $Al'''Cl'_3$.
 Aluminium sulphate, $Al'''_2(SO_4)'''_4$.

A simple plan for writing a formula when one knows the valencies of the radicles concerned, is first to write the formulæ of the radicles side by side, indicating their valencies by dashes in the usual manner, and then to insert the number against each radicle. Let us suppose that we wish to write the formula for phosphoric oxide.

First write the symbols of phosphorus and oxygen side by side ; thus :—

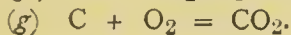
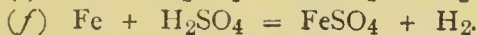
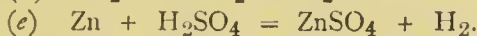
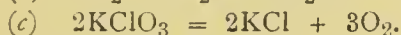
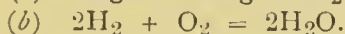


Then the numbers of the atoms will be inversely as their valencies ; thus :—



It must not be forgotten, however, that radicles do not always exert their maximum valency, and that consequently this rule, though useful, will not by itself always lead one right (see 104). It must be supplemented by constant and careful study of the formulæ met with in the course of your reading.

Exercises. 10. Read the following equations, giving the names, number of molecules, weights, and volumes corresponding to the various formulæ :—



CHAPTER IX

CLASSIFICATION OF THE ELEMENTS. ACIDS, BASES AND SALTS

109. Metals and non-metals. It is usual to divide the elements into two great groups known respectively as the *metals* and the *non-metals*. Every one has some idea of the physical characteristics of a metal. We think of a metal as a heavy substance which can readily be burnished and then exhibits metallic lustre, like silver, tin, and gold ; we know that some metals, notably copper and silver, are good conductors of electricity and heat ; that many of them can be drawn into fine wire, or be hammered into thin sheets, that is, that they

are apt to be *ductile* and *malleable*. On the other hand some of the elements, for example oxygen, hydrogen, sulphur, phosphorus and carbon, are notably deficient in all these qualities. These latter elements, and those which resemble them, are called *non-metals*. It is not always easy to say whether a given element should be classed as a metal or a non-metal, for some elements, e. g. arsenic, exhibit some of the qualities which are characteristic of each class.

Let us see whether the members of the two groups differ in their chemical properties as well as physically.

EXPERIMENT 77. To compare the oxides of metals with those of non-metals. Burn fragments of sulphur, phosphorus, carbon, sodium and potassium in clean deflagrating spoons held over a few cubic centimetres of water placed in gas jars (Fig. 40). In each case shake up the product with the water, taste the solution cautiously, and examine its action upon red and blue litmus solution. You will find that solutions of the oxides of carbon, sulphur, and phosphorus redden blue litmus, have no effect on red litmus, and that those of sulphur and phosphorus possess a sour taste. On the other hand, you will find that the oxides of sodium and potassium have no effect on blue litmus, turn red litmus blue, and taste somewhat like soap.

Next examine the action of dilute solutions of oxide of calcium (lime), oxide of barium, oxide of magnesium, oxide of iodine, and oxide of boron, on litmus in a similar manner. You will find, as before, that solutions of the metallic oxides are *alkaline* to litmus, i. e. turn red litmus blue, and that the non-metallic oxides give solutions which are acid.

Here then is a distinct *chemical* difference between metals and non-metals: the oxides of the former tend to form alkaline solutions; the oxides of the latter tend to form acid solutions. This difference between the oxides of metals and of non-metals was first pointed out by Lavoisier.

Of course insoluble oxides, like iron rust (Fe_2O_3), do not produce alkaline solutions, but many of these insoluble oxides, like the soluble alkaline oxides, possess the power of neutralizing acids and forming salts. It is this power of forming *basic oxides*, that is oxides which neutralize acids and form salts, which is characteristic of the metals as a class, rather than the power of forming oxides which are actually soluble and alkaline*.

* The student will learn later that the oxides of metals are not all basic.

EXPERIMENT 78. To study the action of the metals on acids. Place small fragments of zinc, iron, aluminium and magnesium separately in dilute sulphuric acid, also place fragments of iron, zinc, tin and magnesium in hydrochloric acid, and examine the gas given off. You will find that the metal dissolves in every case, and that hydrogen is evolved. If you evaporate the solutions thus obtained they will leave residues which may be crystalline, and which consist of salts formed through the replacement of the hydrogen of the acid by the metals, as explained below :—

Zinc (Zn) and dilute sulphuric acid (H_2SO_4) give zinc sulphate (ZnSO_4) and hydrogen.

Iron (Fe) and dilute sulphuric acid (H_2SO_4) give iron sulphate (FeSO_4) and hydrogen.

Aluminium (Al) and slightly diluted sulphuric acid (H_2SO_4) give aluminium sulphate (Al_2SO_4) and hydrogen.

Magnesium (Mg) and dilute sulphuric acid (H_2SO_4) give magnesium sulphate (MgSO_4) and hydrogen.

Zinc and hydrochloric acid (HCl) give zinc chloride (ZnCl_2) and hydrogen.

Iron and hydrochloric acid (HCl) give iron chloride (FeCl_2) and hydrogen.

Tin (Sn) and hydrochloric acid (HCl) give tin chloride (SnCl_2) and hydrogen.

Magnesium (Mg) and hydrochloric acid (HCl) give magnesium chloride (MgCl_2) and hydrogen.

If you treat other elements, such as copper, lead, carbon, sulphur and phosphorus with nitric or sulphuric acid, you will find that though many are attacked more or less readily, either by weak or by strong acid, the metals alone yield saline substances.

Here then we have another chemical difference between metals and non-metals: many of the former readily replace the hydrogen of acids, forming salts, whilst non-metals will not do so.

As we proceed we shall meet with other chemical differences between the members of the two classes. For example, the metals do not, as a rule, form well-defined compounds with hydrogen, but they readily form stable compounds with chlorine, bromine, iodine, and fluorine and, generally speaking, show great affinity for the non-metals. On the other hand, the non-metals do not replace the hydrogen of acids, but they frequently form stable hydrides, and though

they combine with chlorine, bromine, and iodine, the compounds formed are very apt to be decomposed by water.

EXPERIMENT 79. To study the electrical relations of metals. Set up the galvanic battery used for decomposing water (39), pass the current through acidulated water as before, and mark the electrode at which the hydrogen makes its appearance. Then, using electrodes made of gas carbon, pass the current through solutions of copper chloride, tin chloride, and mercuric chloride, and also through some lead chloride melted in a crucible. You will find that in every case the metal appears at the same electrode as hydrogen, and that a gas with an unpleasant odour (chlorine) is given off at the other electrode. A wider scheme of research would show that whenever a compound of hydrogen, or of a metal, with a non-metal or an acid radicle is decomposed by electricity, the metal makes its appearance at the negative electrode, and the non-metal at the positive electrode. Metals and non-metals are said to be electro-positive and electro-negative respectively.

If we were to examine the electro-chemical relations of all the chief elements we should find it possible to arrange them in such an order that every element in the series would be negative to all that succeed it, and positive to all that precede it. The following would be the *approximate* order of a number of them :—

Negative: O, S, N, F, Cl, Br, I, P, As, B, C, H, Pt, Hg, Ag, Cu, Bi, Sn, Pb, Co, Ni, Fe, Zn, Mn, Al, Mg, Ca, Ba, Sr, Na, K :
Positive.

If we now consider all the elements which come *before* hydrogen in this list, we shall find that, as a class, they are those which form acidic oxides (see Expt. 77), and which are deficient in those qualities, such as high density, conducting power, and metallic lustre, which we associate with the metals. On the other hand, we shall find the elements which follow hydrogen are those which are distinguished for their lustre when polished, for the readiness with which they may be drawn into wire (ductility) or beaten into thin sheets (malleability), for their conducting power and high density; and which chemically are distinguished by their basic oxides, and by the readiness with which they displace the basic hydrogen of acids.

Looking at the matter broadly, therefore, we may conveniently divide the elements into these two groups, viz.—

The *metals*, which are electro-positive to hydrogen, form basic oxides, and replace the hydrogen of acids to form salts, and which usually

possess in a more or less marked degree the physical properties referred to above. Secondly, the *non-metals*, which are electro-negative to hydrogen, yield, as a rule, acidic oxides, form compounds with hydrogen that are comparatively stable and often distinctly acidic, and which do not exhibit conducting power, ductility, malleability or metallic lustre in any marked degree.

The ideal metal would have the properties mentioned above, and some others, such as the power of decomposing water, but no single metal exhibits *all* the properties which we think of as metallic, and many metals exhibit some property or properties which seem to be characteristic of the non-metals. Thus sodium and potassium (350 and 359) are notably metallic in many of their characters, but their densities are low ; gold has the typical physical qualities of a metal, but its hydroxide dissolves in alkalis, forming salts called aurates, and gold has no action on water ; and chromium forms volatile saline compounds with chlorine, and two basic oxides, but it also forms an acidic oxide, from which chromic acid and the chromates are derived (483 to 485).

Hydrogen, it will be perceived, stands alone. Its electrolytic relation to the non-metals, the readiness with which it is replaced by metals, and its other qualities induce one, however, to place it rather among the metals than in the other class.

Metalloids. This name has been applied to certain elements which do not exactly fall into place either among metals or the non-metals. Arsenic (267) and antimony (459) belong to this ill-defined group.

ACIDS, BASES AND SALTS.

110. The oxygen theory of acids. We have seen that the non-metals may be distinguished from the metals by the fact that their oxides are usually *acidic*, or yield acids when dissolved in water, whilst those of the latter are more often basic. This circumstance formerly led chemists to believe that the inorganic acids were the oxides of non-metals, oxygen being the acidifying principle common to them all ; that inorganic basic substances were the oxides of metals, and that salts were formed by the union of acidic oxides with basic oxides. Accordingly the substances represented by the formulæ P_2O_5 , CO_2 , and SO_3 were named phosphoric acid, carbonic acid, and sulphuric acid respectively, and their compounds with metallic oxides, such as lime (CaO), were given names and formulæ

such as the following—phosphate of lime $3\text{CaO}, \text{P}_2\text{O}_5$; carbonate of lime CaO, CO_2 ; sulphate of lime CaO, SO_3 *.

The theory that all acids and bases contain oxygen did good service in various ways, and especially by directing attention to the probability that the bases potash and soda were compounds, because it encouraged chemists to persist in the efforts to resolve these substances into their elements, which culminated in the great discovery of sodium and potassium by Sir Humphry Davy; but it did not long survive Davy's subsequent discovery of the nature of chlorine and hydrochloric acid.

It has long been known that when common salt is gently warmed with strong sulphuric acid a colourless fuming gas is evolved, which dissolves freely in water, yielding the acid liquid formerly known as 'spirit of salt,' but now called 'hydrochloric acid.' In the days of Lavoisier, and of his immediate successors, the composition of this gas was unknown, but in accordance with the *oxygen theory of acids* it was supposed to contain oxygen combined with a hypothetical substance called *murium* † (from *muria* which means sea-salt).

In the year 1774 Scheele discovered that when hydrochloric acid is warmed with the mineral *pyrolusite*, which contains some black oxide of manganese, it evolves a yellowish-green stinking gas which attacks metals vigorously, and dissolves in water, yielding a solution which produces oxygen and muriatic acid ‡ when it is exposed to sunlight. This gas, now known as chlorine, was for a considerable period called oxymuriatic acid, in the belief that it must be a compound of oxygen and muriatic acid, though the presence of these substances in it had never been actually demonstrated.

In 1810 Sir Humphry Davy described a number of remarkable experiments made by him in order to detect, if possible, the oxygen supposed to exist in oxymuriatic acid (chlorine). His results showed that carbon may be heated to whiteness in oxymuriatic acid without any oxide of carbon being produced, and without the carbon undergoing any change; that the gas is in no way altered when it is submitted to strong discharges of electricity from a Leyden jar for several hours in succession; and that no oxygen can be found in the substances produced when tin or phosphorus combine with oxymuriatic acid, which they do readily and completely.

* The exact formulæ used were not always identical with those we should give them to-day.

† This hypothesis has been called the *murium theory*.

‡ The old name for hydrochloric acid.

According to Gay-Lussac's law, which had been established before 1810, one volume of oxymuriatic acid, if it be an element, should combine with one volume of hydrogen to form two volumes of muriatic acid. Now the results of experiments made by Davy's predecessors appeared to show that more than this proportion of oxymuriatic acid was required, and some of the earlier workers, though not all, stated that water was among the products of the reaction. Davy, who dried his gases carefully, also found that a slight contraction occurred when the two gases were exploded together, but he noticed that its amount diminished in proportion as the gases were free from oxygen and water. And further he and his brother showed that when measured quantities of muriatic acid were made to act on metals such as tin, potassium, or zinc, they yielded about half their volume of hydrogen, together with muriates* which he had previously prepared by combining metals with oxymuriatic acid itself, and in which he had been unable to detect the presence of oxygen. In short, Davy showed that in no experiment had oxygen ever been liberated either from oxymuriatic acid itself, or from any of its compounds, and he contended that, since it could not any longer be regarded as an oxide, had not been decomposed, and did not correspond in its properties to any known group of compounds, it must be classed among the elements. From the facts before him he concluded :—

1. That oxymuriatic acid contained no oxygen, but was an element.
2. That hydrochloric acid was a compound of oxymuriatic acid and hydrogen, and contained no oxygen.

In time Davy's views came to be widely adopted, and after the discovery of iodine (163) and bromine (156), which also produce acids when combined with hydrogen, it was generally admitted that substances free from oxygen may undoubtedly possess the properties of true acids.

111. The hydrogen theory of acids. The discoveries of Davy introduced some temporary confusion. It was no longer possible to regard oxygen as the one acidifying principle, since it shared its power of generating acids with chlorine, bromine, iodine, and some other substances †. In 1813 Davy noticed that oxide of iodine (I_2O_5) only acquires acid qualities after it has been dissolved in water; and later Liebig (b. 1803, d. 1873) also directed attention to this point,

* Chlorides.

† It had previously been observed that prussic acid (286) contains no oxygen, but the importance of the observation had been overlooked.

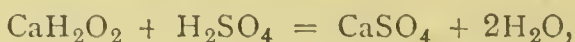
and suggested that if it be assumed that the oxyacids are formed by the union of acidic oxides with water (H_2O), acids might be defined as particular compounds of hydrogen, in which the latter can be replaced by metals—a classification which includes such acids as hydrochloric acid as well as sulphuric acid, and all those which contain oxygen.

All substances which contain hydrogen are not acids. This was quite understood by Davy and Liebig; hydrogen only forms acids, or becomes acidic, when combined with certain atoms, such as those of chlorine and bromine, or groups of atoms like the radicle SO_4 of the sulphates. It is always difficult to define, but we may say provisionally that:—

An acid is a compound of hydrogen with an electro-negative atom or group of atoms (Expt. 79), its hydrogen being replaceable, either entirely or in part, by metals when they are presented to it in the form of hydroxides, a salt and water being produced. It will be perceived, however, that this definition remains incomplete so long as the term *salt* remains undefined.

112. Basic oxides and bases. The great majority of the elements form oxides. Many of the oxides of the non-metals, as we have just learnt, unite with water, and the hydrates so formed are commonly acidic. When the oxide of a metal unites with water it may form a substance which is capable of acting with an acid in such a way that part or the whole of the hydrogen of the acid is replaced by metal. These latter substances are termed *bases*, and the oxides from which they are formed are *basic oxides*.

Quicklime, or oxide of calcium (CaO), for example, readily unites with water (H_2O) to form calcium hydroxide, or slaked lime (CaH_2O_2). This is a base, and if it be added to sulphuric acid somewhat diluted with water the following reaction ensues:—



in the course of which a salt (CaSO_4) is formed by the replacement of the hydrogen of the acid (H_2SO_4) by calcium, water being also produced.

Some of the bases, for example sodium hydroxide (NaHO) and potassium hydroxide (KHO), are very soluble, strongly alkaline, caustic substances; others, like calcium hydroxide ($\text{Ca}(\text{HO})_2$) and barium hydroxide ($\text{Ba}(\text{HO})_2$), are slightly soluble, alkaline, earthy substances; whilst yet others, for example alumina ($\text{Al}_2(\text{H})\text{O}_6$) and ferric

hydroxide ($\text{Fe}_2(\text{HO})_6$), are practically insoluble in water and without action on litmus.

113. Salts. We have already learnt that salts may be made by neutralizing acids with bases (112), and by replacing the hydrogen of acids with metals (Expt. 78). Many of them are soluble and crystalline. They are, with some exceptions, more or less neutral to litmus, and have neither the sour taste of the acids nor the caustic qualities of the strong alkalis, but usually possess either a cool saline taste, like that of common salt, or, in the case of salts of the heavy metals, a distinctly metallic flavour.

Experiments to verify the above.* Taste very cautiously minute fragments of nitre, carbonate of soda, borax, common salt, phosphate of soda, sulphate of iron and sulphate of copper. As many salts are poisonous, only those mentioned may be tasted.

Then examine the action of the same salts on red and blue litmus, and draw up a table showing which have a saline taste and which a metallic flavour, which are really neutral to litmus paper, which alkaline and which slightly acid.

Since salts are derived from acids by replacing their hydrogen by metals, it follows that just as there are acids which contain oxygen and others which do not, so there must be salts containing oxygen, and others which do not contain that element, common salt (NaCl) being an example of the latter and smaller class, and potassium sulphate (K_2SO_4) an example of the former.

The constitution of salts of the oxyacids. See sulphuric acid (199).

114. Acid salts. Since sulphuric acid (H_2SO_4) contains two atoms of hydrogen in every molecule, and is only neutralized when both have been replaced by metal, the student may wish to ask what would happen if we added to some sulphuric acid just half as much alkali as would be required to neutralize it. Should we produce some of the salt Na_2SO_4 , and leave half the acid unaltered, or should we produce a salt of intermediate composition corresponding to the formula NaHSO_4 , and if we produced the latter salt what would it be like? Would it resemble a free acid or a neutral salt?

EXPERIMENT 80. To study the behaviour of alkalis with sulphuric acid. Take 10 grams of sulphuric acid, dilute it with water, neutralize it with solution of caustic soda or of sodium carbonate, adding the alkali gradually from a measuring cylinder, and noting how much is required; then add half the required quantity of alkali

* These experiments need only be made by those to whom the phenomena are not already familiar.

to another portion of 10 grams of sulphuric acid, and evaporate both solutions till they yield crystals.

Examine the crystals produced in each case, noting their taste, solubility, and action on litmus. Then add small quantities of each salt and also of sulphuric acid to some carbonate of soda. Notice that whilst the neutral salt has no action, the other acts like sulphuric acid, setting free carbon dioxide in considerable quantities.

Next heat small portions of the three substances with table salt, and notice that whilst the neutral salt is again without action, the other, and also sulphuric acid, sets free a colourless fuming acid gas in considerable quantity (hydrochloric acid, see 141).

These results show us that when sulphuric acid is mixed with only half as much soda as is required to produce the neutral sulphate (Na_2SO_4), a crystalline substance is formed which very much resembles the original acid in its chemical properties, and as this contains only half as much sodium as the neutral salt, we may conclude that it is a new salt, intermediate in composition between sulphuric acid (H_2SO_4) and sodium sulphate (Na_2SO_4), viz. the salt NaHSO_4 . Such a salt as this is called an *acid salt*.

Basicity of acids. It is evident that any acid which contains more than one atom of replaceable hydrogen in its molecule may produce an acid salt. Such acids are said to be dibasic, tribasic, &c.; those which contain only one replaceable atom of hydrogen in each molecule are monobasic. (See also 199 and 258.)

Exercises. 1. Write the formulæ of the possible salts of sulphurous acid (H_2SO_3), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), phosphoric acid (H_3PO_4), carbonic acid (H_2CO_3), and endeavour to give them their names.

2. Acid sodium sulphate may be made by gently warming sulphuric acid with sodium sulphate (Na_2SO_4). Calculate how much acid you must use to convert 100 grams of sodium sulphate into acid sulphate, and how much acid salt you will obtain.

CHAPTER X

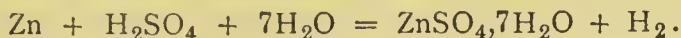
QUANTITATIVE STUDIES CONCERNING SALTS

115. The chief methods of making salts. The following experiments afford examples of some of the chief general methods by which salts may be prepared. They should be performed by the student,

who should endeavour to prepare the quantities mentioned in the instructions, calculating the quantities of material required in each case from the equations. By following this plan he will avoid wasting materials, and gain some experience in applying chemical symbols to one of their proper purposes.

EXPERIMENT 81. To make soluble salts.

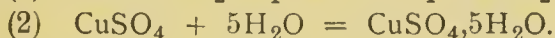
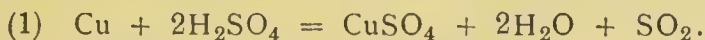
I. To make zinc sulphate by the action of zinc on sulphuric acid. Make 10 grams of this salt :—



Add excess of the metal, in the form of scraps or filings, to the calculated quantity of sulphuric acid diluted with eight or ten times its volume of water. When the action ceases*, filter the solution whilst still hot, wash the filter paper with a little hot water and add the washings to the first filtrate. If crystals do not form on cooling, concentrate the solution. When crystals have formed, collect them on a filter, press them, first on the filter, and then between folds of bibulous paper, to dry them. Then weigh them. They will weigh less than 10 grams, because some of the salt will remain in the mother liquor, and some of this is absorbed by the bibulous paper. Evaporate the mother liquor on a water bath, or over a very small flame. It will then deposit more crystals as it cools, though the weight of the salt will still fall somewhat short of 10 grams.

In subsequent attempts to prepare soluble salts by this method you must endeavour to allow for the error here pointed out.

II. To prepare copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) from metallic copper and sulphuric acid. Make about 10 grams of this salt :—



Heat rather more [why more ?] than the required weight of metallic copper with a moderate excess of strong sulphuric acid in a dish†. When the copper has disappeared, decant the remaining acid from the dirty-looking sediment of impure copper sulphate‡, dissolve the latter in a little boiling water, filter and concentrate the solution, and stand it aside to crystallize. Drain the crystals and evaporate the mother liquor to obtain a further crop. Then dry the crystals in the air and weigh them.

* A small dark residue will probably remain from the zinc; this is partly composed of lead.

† Notice that sulphur dioxide is given off during this operation.

‡ The sediment owes its dark colour to the presence of copper sulphide.

III. To prepare lead nitrate from metallic lead and nitric acid. Make about 10 grams of the salt $\text{Pb}(\text{NO}_3)_2$.

Dilute some nitric acid with several times its volume of water. Then heat rather more than the calculated quantity of granulated lead with the calculated quantity of the diluted acid. When no more lead will dissolve, evaporate the solution till it yields crystals, and obtain as much of the salt as you can from the mother liquor as before.

Notice that in this experiment, as in the last, the metal does not liberate hydrogen, but that a copious evolution of red nitrous fumes occurs. These are produced at the expense of the acid by reduction (227).

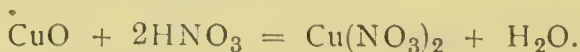
The value of the last mentioned method of making salts is greatly limited by the following circumstances :—

1. That though many metals dissolve in dilute sulphuric or hydrochloric acid, some do not do so, and that many of them can resist the action of some of the weaker acids.

2. That metals which are attacked by strong sulphuric acid, or by nitric acid, usually reduce part of the acid, as in the two previous examples.

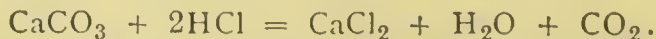
Consequently many salts may be prepared best by dissolving the oxide, hydroxide, or carbonate of the metal in the acid. The following examples will illustrate this method :—

IV. To make 10 grams of nitrate of copper from copper after oxidizing the copper. Roast some copper turnings in a current of air in a tube of hard glass (see *B*, Fig. 42). When the copper is oxidized, dissolve a suitable quantity of the oxide in a moderate excess of nitric acid diluted with water :—



Concentrate the solution very cautiously till it crystallizes on cooling, taking care not to decompose any of the nitrate, and collect, drain, and dry the crystals of nitrate of copper.

V. To make 20 grams of chloride of calcium (CaCl_2) from chalk.



Add chalk (CaCO_3) to the required weight of hydrochloric acid, diluted with water, till no more will dissolve ; filter off the solution of calcium chloride, evaporate it to dryness. Expel the water of crystallization as far as possible by heating the residue strongly till it seems thoroughly dry, then weigh the product.

As you may not succeed in driving all the water from the salt it will probably weigh more than 20 grams.

Salts of the halogens such as chloride of iron, iodide of iron, &c., may be obtained by the direct union of their elements, as also may some sulphides.

EXPERIMENT 82. To make halides by direct combination.

I. To make chlorides by direct combination of metals and chlorine. Heat some iron wire, or iron tacks, at one end *b* of a hard glass tube (Fig. 31) in a current of chlorine (Expt. 107). A dark solid, which dissolves in water, and gives the reactions of a ferric salt (499, II) will condense on the cool parts of the tube. This is ferric chloride (Fe_2Cl_6 or FeCl_3).

If a teacher be at hand to supervise the experiment, a small globule of heated quicksilver may be exposed in a tube to a current of chlorine. A pale flame will occur at the point where the vapour of the mercury meets the chlorine, and a white sublimate, 'corrosive sublimate' (HgCl_2), will condense on the cooler parts of the tube.

II. To make iodide of iron by direct combination. Warm some iron wire gently with a few crystals of iodine and some water in a flask till the iodine has disappeared. The solution will contain ferrous iodide, but it is difficult to obtain the pure salt in the solid state.

III. To prepare iodide of mercury (HgI_2) by direct combination. Place one gram of quicksilver with the proper proportion of iodine in a mortar, moisten them slightly with rectified spirit, and rub them together vigorously with a pestle. As the spirit evaporates, a dry red powder will be formed. This is mercuric iodide (HgI_2). If the mercuric iodide be heated in a test tube it will sublime, yielding beautiful yellow crystals which soon assume a fine red colour.

Repeat the experiment, using half as much iodine. A dark green iodide (Hg_2I_2) will be formed.

INSOLUBLE SALTS. EXPERIMENT 83. Making insoluble salts by precipitation. If we mix solutions of two soluble salts, AB and $A'B'$, which can form an insoluble salt AB' and a soluble salt $A'B$ by double exchange, as in the following equation:—



then the salt AB' will separate as a precipitate and the salt $A'B$ will remain in solution.

For example, silver nitrate ($\text{Ag}(\text{NO}_3)$) and sodium chloride (NaCl)

are both soluble in water, and so is sodium nitrate (NaNO_3), but silver chloride (AgCl) is insoluble. Therefore we can obtain silver chloride (AgCl) as a precipitate, by mixing solutions containing silver nitrate (AgNO_3) and sodium chloride (NaCl) in equivalent proportions. Thus :—



As it is not easy to a beginner to remember which salts are insoluble, a solubility table for some of the chief salts is given on p. 141.

When compounds are prepared by precipitation care must be taken to avoid producing *two* insoluble substances. This can usually be prevented by employing the sodium or potassium salt of the required acid, for most sodium and potassium salts are soluble, and by taking a nitrate or acetate of the required metal.

Since acids and bases are formed by the union of acidic and basic oxides with water, and since acids and bases interact to form salts, we can obtain salts by the direct union of basic and acidic oxides, but the method is not often employed.

Additional Exercises for the Student. These exercises should be performed in the laboratory by the student. A few hours spent at such work is most helpful, especially to those who are not very quick at arithmetic, and of much greater educational value than a similar amount of time spent upon purely arithmetical exercises in the use of chemical symbols.

1. Prepare 2 grams of nitrate of silver.

From the formula $\text{Ag}(\text{NO}_3)$ calculate the amount of silver required.

$$\text{Ag} = 107. \quad \text{N} = 14.$$

Weigh out the required quantity of silver.

Dissolve it in two or three times its weight of nitric acid diluted with a little water.

Evaporate the solution cautiously on a sand bath till it is dry, stirring it gently with a rod to expel water and excess of acid.

The product should be a white soluble solid. It must not have a dark colour nor look like silver. Weigh it. Preserve the specimen.

2. Prepare as nearly as you can 25 grams of nitric acid, using the theoretical proportions of cubical nitre (NaNO_3) and sulphuric acid, and ascertain how much acid you obtain and how much you lose.

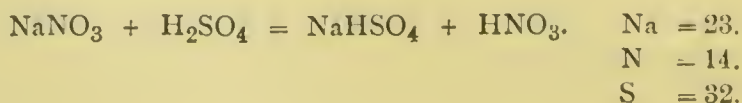


TABLE OF SOLUBILITIES OF SALTS IN WATER.

	K	Na	Am	Mg	Ba	Sr	Ca	Fe ^{III}	Al	Cr	Zn	Mn	Ni	Co	Hg ^{II}	Pb	Bi	Cu	Cd	Sb	Sn ^{II}	Sn ^{IV}	Ag	Hg ^I
Nitrate .	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S ⁺	S	S ⁺	S	S	...	...	S	S	S ⁺
Acetate .	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	...	S	S	S	S
Chlorate .	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	...	S	S	S	S
Chloride .	S	S	S	S	S	S	S	S	S	*	S	S	S	S	S	S	S ⁺	S	S	S ⁺	S ⁺	S	...	...
Bromide .	S	S	S	S	S	S	S	S	S	*	S	S	S	S	S	S	S ⁺	S	S	S	S ⁺	S	...	...
Iodide .	S	S	S	S	S	S	S	S	S	*	S	S	S	S	...	S	...	...	S	S	S	S	...	...
Sulphate .	S	S	S	S	...	...	S'	S	S	S	S	S	S	S	S ⁺	...	S ⁺	S	S	...	S	S ⁺	...	...
Oxide .	S	S	S	...	S'	S'	S'	S	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Sulphide .	S	S	S	...	S	S	S**	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Phosphate	S	S	S	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Carbonate	S	S	S	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Oxalate .	S	S	S	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	S	...	...
Silicate .	S	S	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Arsenate .	S	S	S	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Borate .	S	S	S	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

+ Readily decomposed by water. S' Slightly soluble. S Soluble. ... Insoluble or not known.
 * CrCl₂, CrBr₂ and CrI₂, soluble; CrCl₃, CrBr₃, insoluble if pure. ** See 357 however.

Place the calculated quantities of nitre and acid in a retort (Fig. 14), and distil off as much of the acid as you can into a *weighed* receiver immersed in cold water.

Reweigh the receiver and acid to learn the weight of the acid collected.

If your result is wrong inquire about the source of error.

3. Make 40 grams of iron sulphate in crystals.

This salt when in crystals contains water of crystallization. Its formula is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.



Calculate how much iron and acid are required.

Place the calculated quantity of acid (containing 10 grams H_2SO_4 in 100 c.c. of water) in a dish. Add rather more than the calculated quantity of iron filings and leave them together for some hours.

Filter the solution from the residue, which consists chiefly of carbon, and evaporate till the liquid crystallizes on cooling.

Let the solution cool and drain off the *mother liquor* from the crystals.

Evaporate the mother liquor to obtain a further crop of crystals; add these to the first crop, weigh and preserve them.

A little iron sulphate left in the liquor from the second crop may be obtained by cautiously evaporating it.

4. Prepare 30 grams of nitrate of lead from litharge (PbO).



Calculate how much litharge is required.

Weigh out the necessary quantity of litharge in a state of powder.

Add it to rather more than sufficient nitric acid (allowing for the fact that the acid contains about 65 per cent. of HNO_3) diluted with several volumes of water.

Warm them together, adding water if necessary to dissolve all the salt.

Then decant or strain the hot liquid if it be not clear.

Allow it to cool and crystallize as before.

Recover as much of the salt as you can from the mother liquor, add it to the rest and find the total weight of salt obtained.

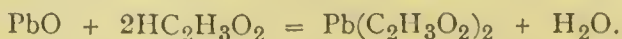
5. Make sugar of lead (acetate of lead) from vinegar.

The acetic acid in vinegar is very far from pure. It can, however, be separated from impurities by distilling it.

Take 200 grams of vinegar, distil two-thirds of it from a retort.

Vinegar contains about 5 per cent. of acetic acid. Let us assume that you have distilled off the whole of this. Then you will have ten grams of acetic acid.

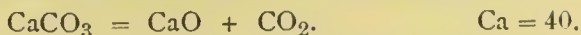
Calculate how much litharge (PbO) will act with this weight of acid from the equation



Digest rather more than the necessary quantity of litharge in the acid; decant the solution; evaporate cautiously on a sand bath and allow to crystallize, &c.

Many oxides are made by heating nitrates or carbonates of the metals.

6. Make 3 grams of quicklime (calcium oxide, CaO) from marble.



Weigh out the required quantity of marble in small pieces.

Heat it as strongly as possible in a muffle furnace, or with a blow-pipe, in an open crucible, till its weight becomes constant.

Then see if it is slightly soluble and alkaline.

Also if it any longer gives off CO_2 with acids.

Expose your lime to the air for a day or two and observe what happens.

7. Make 2 grams of oxide of copper from the nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$,

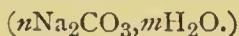


Weigh out the required quantity of copper nitrate.

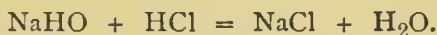
Heat it first gently, then strongly, in a crucible till it gives off no more red fumes (NO_2).

Weigh and preserve the product.

8. Find how much Na_2CO_3 is contained in 10 grams of soda crystals by drying them, and calculate from your results the value of n and m in the formula



9. Make 10 grams of common salt.



Calculate how much of the acid is required*.

Take the required quantity of acid.

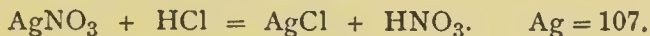
Neutralize it with soda.

Evaporate in a weighed dish.

Weigh your product and preserve it. It should be clean and white.

10. Make one gram of silver chloride.

This is insoluble, so you make it by precipitation.



Calculate the required weight of silver nitrate.

Weigh it out.

Dissolve it in water.

Add excess of hydrochloric acid.

Collect the precipitate on a filter; wash till the washings are no longer acid.

Dry, and preserve the salt after weighing it.

11. Obtain 5 grams of metallic copper by reducing the oxide with hydrogen or coal gas.



Calculate how much copper oxide (CuO) will yield ten grams of copper.

Weigh out the necessary quantity of copper oxide.

Put it in a glass tube (combustion tube) with narrow ends; heat it in a current of coal gas or hydrogen until it is converted into copper.

Weigh and preserve the product.

12. Make 4 grams of iron by reducing iron rust (Fe_2O_3) in a similar way.

* This must be obtained from the teacher.

VOLUMETRIC EXERCISES WITH ACIDS AND ALKALIS.

(116) Acidimetry and alkalimetry.

For the succeeding experiments, the following apparatus will be needed:—A stoppered cylinder graduated in cubic centimetres and holding one litre.

A stoppered flask, which holds 500 c.c. or 1,000 c.c., when filled to a mark on the neck. A similar flask, holding 100 c.c.

Pipettes delivering 5 c.c., 10 c.c., 20 c.c., 25 c.c., and 50 c.c. respectively.

A *burette*. That is, a glass tube graduated in sections of equal capacity, say tenths of cubic centimetres, and provided with a stop-cock, or contracted at one end and provided with a piece of india-rubber tube and a pinch-cock.

A retort stand and clamp, or a burette stand.

It is not so important that these pieces of apparatus shall measure cubic centimetres, &c., correctly, as that they shall agree with one another. Thus the volume of liquid delivered by the 50 c.c. pipette should exactly fill the 100 c.c. flask by two operations. The volume of liquid delivered by the 25 c.c. pipette should be just five times as great as that delivered by the 5 c.c. pipette. The student must therefore begin by calibrating his apparatus.

EXPERIMENT 84. **To calibrate the burette, &c.** Obtain a small dry flask and weigh it; fill your burette with water, run off its contents in portions of 5 c.c., and weigh each of them. Then make out a list of your results. If the burette be a fairly good one, the weight of 5 c.c. of water will be nearly 5 grams in every case (28). If there be great differences you must either get a new burette, or make suitable corrections in your subsequent work.

You cannot, as you will have discovered, measure 5 c.c. very accurately from a burette. You will draw off rather more or rather less than 5 c.c. nearly every time. Still, the error need not be great if you attend to the note which follows. The influence of this error of observation is large if the volume measured be small, say 1 c.c., and it is correspondingly reduced if you draw off a large volume, say 50 c.c. Therefore it is best to measure comparatively large volumes rather than small ones if circumstances permit you to do so.

When you are compelled to measure small volumes you must,

if it be possible, make several measurements and take the mean result.

In reading the burette observe that the liquid has a curved surface; this is called its *meniscus*. If you hold a sheet of white paper behind it, a dark line will appear. It is a good plan to read from the lower edge of this dark line, taking care that your eye, the lower edge of the dark line, and the mark on the burette are all at the same level at the moment of reading.

Exercise. Deliver 1 c.c. of water from your burette and find how far the weight of 1 c.c. of water thus obtained departs from 1 gram.

Deliver 50 c.c. of water, weigh it, and calculate the weight of 1 c.c. of water from your result.

Compare the two values thus found for the weight of 1 c.c. of water.

Repeat the above experiments and notice which pairs of results agree most closely.

Fill each of your pipettes to the mark, run its contents into a weighed beaker or flask, allowing the pipette to drain for five or six seconds, with its tip just below the surface of the liquid. (N.B.—Do not throw out the last drop.) Then weigh the beaker and its contents, and reject any pipette which is not in agreement with the rest, or, if you cannot replace it, make a note of the error.

Remember that you do not need to know how much liquid a pipette or burette *holds*, but how much it *delivers*.

Compare the capacities of your measuring flasks and measuring cylinder with those of the pipettes, either by weighing them when empty and again when filled to the mark with water; or by transferring water from the 50 c.c. pipette to the flasks. The 50 c.c. pipette should fill the 500 c.c. flask when the contents of the former are emptied into the latter ten times. It should fill a 100 c.c. flask after two such operations, and so on.

When a doctor orders for his patient ten doses of a drug each of 1 grain, the chemist does not weigh out each dose separately, but weighs out 10 grains at once, dissolves the whole in, it may be, 10 ounces of water, and sends it to the patient in a bottle so marked that he can pour out as much of its contents as will contain 1 grain of the drug whenever he wishes to take a dose of his medicine.

This easy method of dividing up soluble solids has long been practised in pharmacy. It was introduced, in more exact forms, into chemical analysis by Gay-Lussac about 1824, and its use was greatly promoted by Friedrich Mohr, the pharmacist, of Coblenz,

who extended the applications of the method, and published a Text-book of Volumetric Analysis. Its usefulness depends on the fact that a dissolved solid spreads itself uniformly throughout a liquid in which it is dissolved, so that if 10 grams of the solid are dissolved in sufficient water to make 100 c.c. of solution and well shaken, each cubic centimetre of the solution will contain exactly 0.1 gram of the solid.

Exercises. 1. Verify the above statement experimentally by dissolving 10 grams of salt in 100 cubic centimetres of water, and ascertaining if measured volumes of the solution contain quantities of salt bearing the same proportions to one another as the volumes of the liquid from which you obtain them.

2. Divide the salt in 10 c.c. of the solution given you into two equal parts without using scales or weights.

3. The salt given you weighs 1 gram; obtain 2 milligrams of it in the solid state in a dish.

4. Say how a pharmacist could obtain the one-thousandth part of a grain of strychnine.

5. If 1 litre of a liquid contains 120 grams of sugar, how much sugar is present in the following volumes:—10 c.c., 45 c.c., 125 c.c.?

ACIDS, ALKALIS, AND INDICATORS.

Take some solution of sodium hydroxide, add *a little* red litmus solution to it, and observe the effect.

Take some solution of sulphuric acid, add a little to blue litmus, and observe the effect.

Make some neutral litmus by adding very dilute alkali to red litmus, or very dilute acid to blue litmus, till it assumes an intermediate neutral tint. Then observe its behaviour with an acid, an alkali, and also with a neutral salt.

If you add sulphuric acid to solution of caustic soda and try to hit the point at which the alkali loses its soapy flavour, but at which it does not yet taste sour, you will find it is exceedingly difficult to do so. And if you make several experiments using the same acid and alkali, you will find that you use different quantities of acid in each case. This is because the sense of taste does not discriminate very well between the two flavours. Now see how much more exactly you can work if you use litmus, as in the following experiment, to *indicate* the

point at which the acid and alkali are in the right proportions to form a neutral salt.

EXPERIMENT 85. To learn whether the proportions in which a given acid and alkali neutralize each other are constant. Measure 10 c.c., 20 c.c., and 25 c.c. of a solution of sodium hydroxide, free from carbonate, into three flasks, and add a few drops of neutral solution of litmus. Then run some dilute solution of hydrochloric acid into each flask of alkali from the burette (using portions of the same acid in every case), until the litmus is just reddened by excess of acid.

Notice how much acid is required in each case, and whether the volumes of acid required bear a constant proportion to the volumes of alkali taken.

In doing these experiments, do not forget that to get good results you must take the mean of at least two experiments in each case, and that these should be rejected if they differ too widely.

Litmus is a most useful indicator but it fails when used with alkaline carbonates, and in certain other cases:—

Add hydrochloric acid, as in the previous experiment, to some solution of sodium carbonate, containing a little litmus, till the liquid turns red. Then boil the solution. It will become blue again owing to the expulsion of the carbonic acid gas. Now add more acid and boil again, repeating the process until the red colour is no longer removed by boiling. You have now completely destroyed the carbonate.

In the presence of carbonic acid, therefore, the liquid to be neutralized must be treated as in the above experiment, or some indicator must be used which is indifferent to the action of carbonic acid gas. Methyl orange and cochineal possess this quality, and the latter is particularly useful if one works by gas-light.

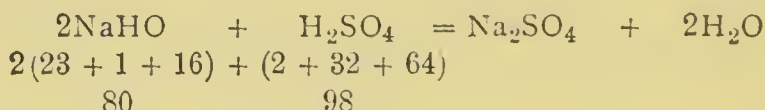
The student should acquaint himself with the action of acids and alkalis on these two indicators, and then repeat the experiment of neutralizing a carbonate, using methyl orange and cochineal in place of litmus.

For this purpose he should use the alkaline solution given him, and the master will tell him when his results are correct.

EXPERIMENT 86. To make a normal solution of an acid. The ordinary dilute solutions of acids and alkalis vary in strength; therefore it is necessary to prepare solutions of known composition for volumetric work.

So far as the experimental work is concerned, it makes no difference whether we use a solution of sulphuric acid, for example, which contains 50 grams of H_2SO_4 in every litre (i. e. 1,000 c.c.), or one which contains 49 grams of H_2SO_4 in each litre. But when we work out our results we find the latter much more convenient than the former. For 49 is a number very simply related to the combining weight of H_2SO_4 , viz. 98, whilst the number 50 does not bear so simple a relation to this quantity.

Let us suppose, for example, that we have found as the result of an experiment that 104 c.c. of a solution of sulphuric acid of the former strength neutralizes 60 c.c. of a solution of soda, NaHO , of unknown strength. Then to find the strength of the soda, we have the following calculation:—



From the equation we see that 98 grams of H_2SO_4 neutralize 80 grams of NaHO .

Therefore 50 grams of H_2SO_4 will neutralize $\frac{80 \times 50}{98}$ grams of NaHO .

That is, 1,000 c.c. of a solution containing 50 grams of H_2SO_4 per litre will neutralize $\frac{80 \times 50}{98}$ of NaHO .

And therefore 104 c.c. of the same solution will neutralize

$$\frac{80 \times 50 \times 104}{98 \times 1000} \text{ grams of NaHO.}$$

But 104 c.c. of acid solution neutralize 60 c.c. of the soda solution. Therefore 60 c.c. of the soda solution contain

$$\frac{80 \times 50 \times 104}{98 \times 1000} \text{ grams of NaHO.}$$

But if the standard acid contains 49 grams of H_2SO_4 per litre, the calculation becomes much simpler. Thus:—

From the equation, we find that 98 grams of H_2SO_4 neutralize 80 grams of NaHO .

Therefore the 49 grams of H_2SO_4 in a litre of the solution will neutralize $80 \times \frac{49}{98} = 40$ grams of soda, and each cubic centimetre will neutralize $\frac{40}{1000} = .04$ gram of NaHO .

Or 104 c.c. of the acid will neutralize $.04 \times 104$ of NaHO .

Exercises. Using the acid given you, which contains 49 grams of H_2SO_4 per litre, find, after the reading the note below:—

1. How much soda, NaHO , is in each c.c. of the solution *A*?
2. How much potash, KHO , is in each c.c. of the solution *B*?
3. How much K_2CO_3 is in 100 c.c. of *C*?

NOTE.—Before you begin your experiment, calculate how much NaHO , KHO , or K_2CO_3 , as the case may be, will be neutralized by each c.c. of the standard acid. Then the product of this quantity multiplied by the number of cubic centimetres of acid used will give you the weight of NaHO , KHO , or K_2CO_3 present in the solution taken for your experiment.

4. Find how much of solution *D* contains 100 grams of NaHO .
5. Find how much KHO there is in 1 gram of the solid *E*.
6. Find the weight of the K_2CO_3 given you (*G*) by volumetric analysis.

Before proceeding obtain some solution of hydrochloric acid containing 10 % of HCl , and with it find:—

7. The percentage of NaHO in *H*.
8. The amount of KHO in 100 c.c. of *I*.

Normal and decinormal Solutions. Solutions containing one equivalent proportion in grams of an acid or alkali in each litre of solution are termed 'normal' solutions. If the quantity is one-tenth of this they are called 'deci-normal' solutions.

It must be remembered that an equivalent weight of an acid contains one atom of replaceable hydrogen. Thus HCl and $\frac{1}{2} (\text{H}_2\text{SO}_4)$ correspond to the equivalent weights of hydrochloric acid and of sulphuric acid.

Again, NaHO and $\frac{1}{2} (\text{CaH}_2\text{O}_2)$ correspond to the equivalents of soda and of calcium hydroxide respectively. For an equivalent of a base contains as much metal as will replace the hydrogen in an equivalent of an acid.

To prepare a normal solution of oxalic acid. Purify some oxalic acid by recrystallizing the commercial acid. Calculate its

equivalent weight from the formula $\text{H}_2\text{C}_2\text{O}_4$. Then find how much crystallized oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) will be required to yield an equivalent weight in grams of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$. Powder and dissolve this weight of the crystals in water in a litre flask, and dilute till the volume of the whole is 1,000 c.c. at the ordinary temperature.

Calculate how much $\text{H}_2\text{C}_2\text{O}_4$ is present in each c.c. of this solution.

NOTE I.—In such work as that which you are about to do, pairs of experiments should be made, and, as some of them may be failures, it will be well to weigh out a sufficient quantity of the substance for four or five experiments, and to make up the solution of this to a certain volume which can afterwards be subdivided. Thus, if 1 gram of a substance is to be used for each trial, you may dissolve about 4 grams of the substance and dilute the solution to 100 c.c.; then 25 c.c. will contain one-fourth of the substance taken.

NOTE II.—If, in any experiment, you find that only one or two cubic centimetres of standard acid or alkali are required, it is best to reject the result obtained and to repeat the work, using a decinormal solution, or taking more of the substance. If your burette is graduated in tenths of cubic centimetres, you may perhaps be able to read to a twentieth of a cubic centimetre, consequently if only 1 c.c. of standard solution be used the experimental error will be very large, viz. 1 in 20; if, however, you dilute some of your normal solution, making it a decinormal solution, then 10 c.c. will be required, and the error will be reduced to 1 in 200.

EXPERIMENT 87. To find the equivalent weight of soda. That is to find how much soda, NaHO , will neutralize as much oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, as contains unit mass of replaceable hydrogen (see 86 and 87). If we take unit mass of hydrogen to be 1 gram, then 45 grams, $\frac{1}{2}(\text{H}_2\text{C}_2\text{O}_4)$, will be an equivalent in grams of oxalic acid. Take about 2 grams of soda dissolved in water, add some neutral litmus, and titrate the alkali with the standard solution of oxalic acid, as in Experiment 85. Then calculate how much soda will be required to neutralize an equivalent, i.e. 45 grams, of oxalic acid. The solution of soda employed for this experiment should be prepared for the student by the teacher.

EXAMPLE. Suppose 30 c.c. of normal acid neutralize 1.2 grams of soda:—

Then since each cubic centimetre of oxalic acid solution contains 0.045 gram of acid, 30 c.c. contain $30 \times 0.045 = 1.35$ grams of oxalic acid.

1.35 grams $\text{H}_2\text{C}_2\text{O}_4$ neutralize 1.2 grams soda,

$$1 \quad " \quad " \quad " \quad \frac{1.2}{1.35}$$

$$\text{And } 45 \quad " \quad " \quad " \quad \frac{1.2}{1.35} \times 45$$

$$= 40.$$

Exercise. Find the equivalent weight of potash in a similar manner, i.e. find how much potash will neutralize 45 grams of oxalic acid.

EXPERIMENT 88. To find the equivalent weight of carbonate of soda. Weigh out about 4 grams of the salt (see Note I) after driving off its water of crystallization, dissolve it in water and titrate the solution, whilst cold, with your normal acid; notice that carbon dioxide is evolved freely when you add the acid. When the solution becomes red, boil it to expel the dissolved carbon dioxide, and when it becomes blue again, add more acid till it is once more reddened, then boil it again, and repeat the treatment until the liquid is permanently reddened. You will then have decomposed all the carbonate.

From the amount of carbonate of soda used and the amount of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) required to neutralize it*, calculate, as before, how much carbonate would be required to neutralize an equivalent weight in grams (45) of oxalic acid. This will be the equivalent weight of the carbonate.

Further Exercises. Obtain some normal solution of sulphuric acid. Since sulphuric acid, H_2SO_4 , contains 2 parts of replaceable hydrogen † in 98 of the pure acid, the normal acid (see above) will contain 49 grams of sulphuric acid in each litre.

1. Calculate how much sulphuric acid there is in each cubic centimetre of normal sulphuric acid.

2. Using the same soda as for Exp. 87, titrate some of it with normal sulphuric acid, and from your result calculate the equivalent weight of the soda, i.e. how much would be wanted to neutralize an equivalent weight in grams of sulphuric acid. Does your result agree with the former one?

3. Find the equivalent weight of carbonate of soda in a similar manner, using normal sulphuric acid and methyl orange as indicator instead of litmus.

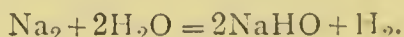
* Remember that each c.c. of the solution of oxalic acid only contains 0.045 gram of real $\text{H}_2\text{C}_2\text{O}_4$.

† It is customary to write the replaceable hydrogen of an acid at the beginning of its formula. Thus the formula $\text{HC}_2\text{H}_3\text{O}_2$ indicates that only one-fourth of the hydrogen in each molecule of acetic acid is replaced when we neutralize the acid with soda or any other alkali.

4. Find the equivalent weight of carbonate of potash, using normal sulphuric acid and methyl orange.
5. Find the equivalent weight of potash in the same manner.
6. Compare the equivalent weights found when you titrate with oxalic acid with those obtained when you use sulphuric acid.

EXPERIMENT 89. To find the equivalent weight of an acid, using an alkali of known strength. The equivalent weight of an acid has already been defined to be 'that weight of the acid which contains unit mass of replaceable hydrogen' (p. 90). We have seen, however, that an equivalent weight of an acid will neutralize an equivalent weight of an alkali. We may therefore, on occasion, determine the equivalent weight of a given acid by finding how much of it is required to neutralize an equivalent weight of an alkali.

There are several modes by which we may prepare standard solutions of alkalis. For example, an equivalent of sodium, Na, will generate an equivalent of soda NaHO if it be dissolved in water



Therefore we may dissolve 23 parts of sodium in spirit of wine, evaporate the spirit and dissolve the residue in sufficient water to make one litre of solution.

Again, 106 parts of sodium carbonate, Na_2CO_3 , contain 23×2 parts of sodium. Therefore 53 parts would neutralize an equivalent of an acid, and 53 grams dissolved in one litre of solution would give us a normal alkaline solution.

Make some normal alkaline solution according to method I or II.

1. Get a clean block of sodium weighing about 1 gram. Weigh it quickly in a well-closed bottle. Cut it up in a dish and throw the fragments one by one into 10 c.c. of rectified spirit. When *all* is dissolved, drive off most of the spirit by heating in a dish on a water bath. Dilute the product to the right volume with water in order to obtain a decinormal solution of soda.

For example—since 23 is the equivalent weight of sodium, 23 grams of sodium would give 1000 c.c. of normal solution of NaHO. And (see p. 90) 2.3 grams would give 1000 c.c. of decinormal soda.

Suppose that you take 1.15 grams of sodium. Then

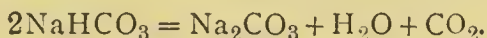
$$\begin{array}{lcl} 2.3 \text{ grams Na give} & 1000 \text{ c.c. decinormal alkali.} & \\ \therefore 1.15 \quad \text{,,} \quad \text{,,} & 1000 \times \frac{1.15}{2.3} = 500 \text{ c.c.} & \text{,,} \end{array}$$

Next, to test the accuracy of your work, measure out 20 c.c. of decinormal acid with a pipette, add litmus and titrate it with the decinormal alkali.

How much decinormal alkali will be required to neutralize 20 c.c. of decinormal acid ?

To get really good results by this method the sodium must be pure, and quite freshly cut when you weigh it.

II. Make some pure sodium carbonate, Na_2CO_3 , by heating the best bicarbonate to dull redness in a platinum dish till it ceases to lose weight :—



Calculate how much of this salt, Na_2CO_3 , must be used to yield a solution containing one equivalent of sodium, as carbonate, in each litre.

Weigh out the calculated quantity of the salt, dissolve it in less than 1 litre of water, and dilute the product to 1 litre.

Test the accuracy of your work by finding whether 30 or 40 c.c. of the standard alkali exactly neutralizes the proper volume of normal acid*.

At the beginning of the exercises on volumetric analysis we calculated the equivalent weight of oxalic acid from its formula, $\text{H}_2\text{C}_2\text{O}_4$; taking as our equivalent the quantity which contains 1 part of replaceable hydrogen, let us now determine this equivalent by experiment instead of calculating it, and see if the two values agree.

Since each litre of the standard sodium carbonate contains one equivalent in grams of sodium; it contains enough sodium to replace one gram of hydrogen, i.e. to neutralize one equivalent in grams of an acid.

Therefore what we have to do is to find how much oxalic acid will neutralize a litre of the normal solution of sodium carbonate.

Weigh out a convenient quantity of oxalic acid, say about 8 grams; dissolve it in sufficient water to make 100 c.c. of solution. Add this from a burette to 30 c.c. of the standard alkali till the latter is neutralized.

Then since each cubic centimetre of the acid liquid contains $\frac{8}{100}$ gram of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, you can easily calculate :—

1. How much $\text{H}_2\text{C}_2\text{O}_4$ was required by 30 c.c. of the normal soda.

* By this time the student should have discovered that when a chemist wishes to prepare a set of standard solutions of acids and alkalis, he must prepare one solution of acid or alkali from the purest materials with the greatest possible care, and then use this as a standard of comparison for the others.

2. How much $\text{H}_2\text{C}_2\text{O}_4$ would be required by 1 litre of normal soda, i. e. by the 1 equivalent in grams of soda in 1 litre of that solution.

Question. Was it necessary to add the acid to the alkali? Would the reverse process have answered equally well? Try this.

EXPERIMENT 90. Finding the strength of an acid or an alkaline substance. It is of course possible to determine the quantity of any given acid or base in a solution containing it by volumetric analysis. And similarly, if we have a solid substance we can dissolve a known weight of it and find how much alkali it contains by finding the amount of alkali in the solution.

EXAMPLE 1. *To find the proportion of sodium carbonate in a crystal of washing-soda, and to find the formula of the salt.*

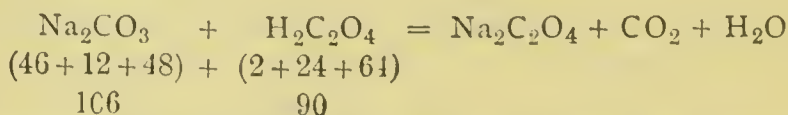
Take a clean dry crystal of washing-soda, powder it, weigh out a convenient quantity, about 30 grams, dissolve this in water and make up the solution to 200 c.c.; titrate 30 c.c. of this solution with normal acid, adding a cubic centimetre of acid at a time. Then take a fresh quantity of alkali, add nearly all the required quantity of acid at once, and finish off the titration carefully.

It is usually judicious to do a pioneer experiment of this kind when you do not know how much volumetric solution will be wanted, for much time may be lost in adding a large volume of a standard solution from the burette drop by drop. About 30 or 40 c.c. is a convenient volume of volumetric solution to use (see Note II, p. 91).

Method of calculating:—

Let us suppose that 20 c.c. of a solution containing 30 grams of soda crystals in 100 c.c. are neutralized by 42.0 c.c. of normal oxalic acid.

From the equation



We see that 90 grams of $\text{H}_2\text{C}_2\text{O}_4$ will neutralize 106 grams of Na_2CO_3 .

But each c.c. of normal oxalic acid solution contains

$$\frac{90}{1000 \times 2} = 0.045 \text{ gram of } \text{H}_2\text{C}_2\text{O}_4, \text{ and therefore will neutralize}$$

$$\frac{106}{1000 \times 2} = 0.053 \text{ gram of } \text{Na}_2\text{CO}_3.$$

Therefore 42 c.c. of oxalic solution will neutralize $0.053 \times 42 = 2.226$ gram of Na_2CO_3 .

Therefore 6 grams of washing-soda must contain 2.226 of Na_2CO_3 , and the rest must be water of crystallization.

Then to find its formula we have :—

$$\text{Na}_2\text{CO}_3 = 2.226 \div 106 = 0.021$$

$$\text{H}_2\text{O} = 3.774 \div 18 = 0.21.$$

But $0.021 : 0.21 :: 1 : 10.$

Therefore the formula of the salt is $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}.$

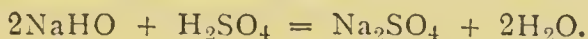
EXERCISE. Find the proportion of potassium carbonate in 100 parts of a sample of the commercial salt.

EXAMPLE 2. *To find the percentage of pure sulphuric acid (H_2SO_4) in commercial sulphuric acid.*

Place some strong sulphuric acid in a small dry bottle of known weight, and weigh the bottle with its contents. Pour about 6 c.c. of the acid slowly into 90 c.c. of water, reweigh the bottle with the residue of strong acid, and when the diluted acid has become cool dilute it further to 100 c.c.

N.B.—You must be very careful not to spill any of the strong acid, *all* that goes out of the weighed bottle must go into the water.

Then titrate measured portions of the diluted acid in the manner previously described, and calculate the proportion of real acid (H_2SO_4) with the aid of the following equation :—



EXERCISE 1. Is the hydrochloric acid given you normal? If not, how much water must you add to 1 litre to make it normal?



EXERCISE 2. Find the strength of the strong solution of ammonia given you.

For convenience sake, Tables and curves have been prepared showing the strengths of solutions of the chief acids, and of ammonia of various densities. Thus in practice if we wish to test the quality of hydrochloric acid when we buy it, we may take its density, and look at the Table or curve to find the corresponding strength, after assuring ourselves that it leaves no residue when evaporated.

EXAMPLE 3.—*Using a table or a curve, find how much strong hydrochloric acid is required to make some decinormal solution, proceeding as follows :—*

1. Find how much water a given 5 c.c. pipette will deliver. Call the weight W .

2. Find how much strong hydrochloric acid the same pipette will deliver. Call this weight w . Then $\frac{w}{W}$ will give you the density of the acid.

3. Find from the Table, or from the curve given at the end of the book, the strength of acid of this density. Weigh out a few grams of it, and calculate to what volume you must dilute it in order to obtain a decinormal solution. Carry out the experiment, and see if 5 c.c. of normal soda will neutralize 50 c.c. of the decinormal acid.

EXAMPLE 4. *To fix the basicity of an acid of known molecular weight* (see also p. 76). When an acid contains one atom of replaceable hydrogen in each molecule, we say it is *monobasic*; if it contains two such atoms, *dibasic*; and so on. And since an equivalent of an alkali contains enough metal to replace one atom of hydrogen in acid by metal, we can use a normal alkaline solution to find the *basicity* of an acid, or a normal acid to fix the *acidity* of a base, provided that we know their molecular weights.

Weigh out some sulphuric acid containing about 70 per cent. H_2SO_4 (its strength may be found from its density by means of the curve which follows p. 134). Dilute it so that each cubic centimetre shall contain the one-thousandth part, in grams, of a molecular weight.

Titrate a measured volume of the solution with normal soda solution.

Calculate how many equivalents of soda are required to neutralize a molecular proportion of the acid.

Make a similar experiment, using solution of nitric acid, or hydrochloric acid, and compare the results obtained.

EXPERIMENT 91. **A method of dealing with basic substances which are insoluble, or only slightly soluble in water. To find the equivalent weight of calcium hydroxide.** Obtain some normal solution of hydrochloric acid.

Prepare some calcium hydroxide by slaking some good lime, made from precipitated chalk, with water, and dry it carefully.

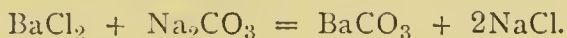
Weigh out about 3 grams of the carefully dried slaked lime, and dissolve it in a measured volume of the normal acid, using about twice as much acid as is actually required for the purpose. Dilute the solution thus obtained to a convenient volume, and titrate the excess of acid in two measured portions of it with normal alkali.

Then if v c.c. of normal acid, in which x of slaked lime have been

dissolved, neutralize v' c.c. of normal alkali, it follows that x grams of slaked lime have neutralized $v - v'$ c.c. of normal acid.

From the data obtained, calculate the required equivalent weight.

EXPERIMENT 92. To find the amount of a salt of barium in a given solution. Take a measured quantity of the given solution, and add a measured but excessive quantity of normal solution of an alkaline carbonate. The barium will be completely precipitated as barium carbonate (BaCO_3), e.g. :—



Filter off the precipitate, wash it with water, mixing the washings with the original filtrate, dilute the whole to a suitable volume, and find how much of the alkaline carbonate remains by titrating portions with normal acid *. Deduct the excess of carbonate from the amount taken, to find how much was used by the barium chloride. Then from this, and using the equation, calculate the amount of the salt in the solution given you.

Ammonium salts. These may be dealt with in an analogous manner, by taking advantage of the fact that ammonia is readily expelled from solutions of its salts by heating with an alkali.

EXPERIMENT 93. To find the amount of ammonium chloride in a given solution. Boil a measured volume of the given solution with a measured excess of normal solution of soda till ammonia is no longer given off. If the residue be not strongly alkaline, add more alkali and reboil. Titrate the excess of fixed alkali with standard acid, and work out your results as in the previous cases.

Ammonium chloride is decomposed by soda in accordance with the following equation :—



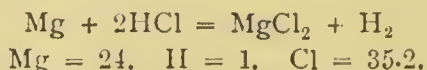
Therefore one molecular proportion of soda will be destroyed by each molecular proportion of ammonium chloride (NH_4Cl) in the solution.

Further exercises for the student. 1. Find the amount of replaceable hydrogen in 73 parts of the acid sulphate of potassium, by neutralizing a weighed quantity of the salt with a standard alkali.

2. Dissolve some magnesium turnings in a known excess of a standard solution of hydrochloric acid. Find how much acid remains by titrating it with

* Or dissolve the washed carbonate in excess of standard acid and titrate the remaining acid with standard alkali.

a standard alkali. Then calculate the weight of the magnesium, and that of the hydrogen liberated.



3. Find whether the salt given you is carbonate or bicarbonate of soda.
4. Dissolve a weighed piece of sodium, using very small fragments at a time, in alcohol; find how much normal acid the alkaline solution thus obtained will neutralize, and deduce the equivalent weight of sodium from your result.
5. Find the strength of the given solution of sulphuric acid, and calculate how much water you must add in order to obtain a decinormal solution.
6. Find the percentage of calcium chloride in a sample of that salt.
7. Endeavour to find the weight of barium chloride and sodium chloride, respectively, in a solution containing these two salts.
Find the proportion of mixed salts in the solution by evaporating a measured volume of it in a weighed dish and reweighing the dish and the salts. Then find the amount of the barium chloride in a measured volume of the solution by a volumetric method. The amount of sodium chloride may afterwards be found by difference.
8. Find the respective percentages of ammonium hydroxide and soda in a solution containing both.
9. Find how much chlorine there is in a gram of ammonium chloride, following the process of Experiment 93, and calculate the amount of ammonium (NH_4) by difference.

OTHER EXERCISES IN VOLUMETRIC ANALYSIS.

Estimating chlorine and silver volumetrically. Dissolve one-tenth of an equivalent (58.2) in grams of pure salt (NaCl) in sufficient water to make 1 litre of solution. Add a few drops of dilute solution of potassium chromate to some of this, then titrate with a solution containing silver nitrate. The precipitate will be white until all the chlorine is thrown down:—



Directly the precipitate acquires a permanent chocolate colour cease adding the silver solution, and from the volume of volumetric solution required, calculate how much silver nitrate was present in the silver solution.

It will be obvious that by using a solution of silver nitrate of known

strength, and a solution of a chloride of unknown strength, the proportion of the latter may be found.

If the solution to be titrated is acid, we cannot use chromate as an indicator, for silver chromate is soluble in acid. In this case therefore the solution must be exactly neutralized, or you may proceed as follows.

Acidify the silver solution with nitric acid, and add the decinormal sodium chloride as before, shaking very vigorously, and allowing the precipitate to subside after each addition. When the addition of a drop or two of sodium chloride solution causes no further precipitation, notice how much has been required. You will find that towards the end of the process the precipitate falls rather slowly, but as soon as excess of chloride has been added the liquid will clear much more easily.

The student should determine the strength of a sample of solution of hydrogen chloride in this manner, using a decinormal solution of silver nitrate.

Exercise on the above. Find the amount of chlorine, by the above method, in a sample of pure sodium chloride, and deduce the equivalent weight of sodium—

(*a*) On the assumption that the equivalent of chlorine is 35.2.

(*b*) On the assumption that the equivalent of silver is 107.1.

A good example of the application of this important method of determining combining or equivalent weights may be found in a subsequent section p. 288.

The oxidizing power of potassium permanganate is made use of in quantitative analysis. Unfortunately, solutions of this salt become gradually weaker when kept, and therefore their oxidizing power must be remeasured at frequent intervals.

The student should now extend his work in volumetric analysis by doing the following, if time permits.

(*a*) Experiment 300, p. 468 (100).

(*b*) „ 301, p. 469 (101).

(*c*) The 'Exercise' following 4, p. 250.

(*d*) „ „ „ 4, p. 326.

SOME GENERAL METHODS FOR PREPARING NORMAL SOLUTIONS OF ACIDS AND ALKALIS.

1. Standard Alkali:—

(a) Dissolve a known mass of sodium in small fragments one by one in alcohol and evaporate the spirit. Dilute so that each cubic centimetre shall contain .04 gram of NaHO.

(b) Prepare pure, dry sodium carbonate Na_2CO_3 by heating the bicarbonate till it ceases to lose weight. Dissolve a known mass of this in water and dilute so that each litre shall contain one equivalent weight in grams of Na_2CO_3 .

2. Standard Acid:—

(a) Determine the density of some sulphuric, nitric or hydrochloric acid. Ascertain its state of concentration from the curve at the end of the book. Then dilute a known quantity of the acid so that each litre may contain an equivalent weight in grams.

(b) Dissolve an equivalent weight in grams of copper sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water; pass electricity through the solution, using Platinum Electrodes, until all the metal is deposited. Then dilute sufficiently to make a normal or decinormal solution. If you weigh the deposited copper you will have a further check on the accuracy of your work.

(c) Hydrochloric Acid gas may be passed into a known weight of water and the gain of weight ascertained (see 141). A solution of known strength made in this way can be diluted so that a normal solution is produced.

The student should note that having prepared a stock of one accurately made normal solution, acid or alkali, he can use this as a 'Control Solution.' For example:—If he has some normal solution of soda made from sodium, he can dilute solutions of ordinary soda, NaHO, or of sodium carbonate, so that measured volumes of these shall neutralize the same quantity of a given acid as an equal volume of the control solution. He will then have normal solution of soda or sodium carbonate. Again, if a given volume of an acid solution will neutralize an equal volume of the normal alkali it must itself be normal.

Similar use can be made of standard solutions of acids prepared by methods *a b c* or made from oxalic acid.

FURTHER EXERCISES,
MOSTLY QUANTITATIVE, IN ANALYSES AND SYNTHESSES,
AND DETERMINATIONS OF COMBINING PROPORTIONS.

In making the following preparations the student should aim at obtaining specimens of 1 gram, 5 grams or 10 grams, according to the value of the material and the circumstances of the case.

EXERCISE A'. To prepare hydrochloric acid.

This gas is usually preserved in solution. To make a little of this solution the instructions on p. 192 must be followed. [What substances could you use in place of common salt?] The more obvious properties of the gas should be noticed, e. g. :

Does hydrochloric acid fume in *dry* air?

„ „ „ „ „ damp air?

What is its action on litmus?

What happens if you pass the gas over a few fragments of sodium heated in a glass tube? To learn this, place the sodium in a piece of hard glass tube drawn out at one end [Fig. 64, p. 194 (114)], attach the other end to the delivery tube *E* [Fig. 63, p. 192 (80)], and proceed as described on p. 194 (114).

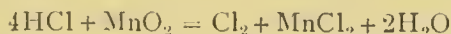
A little hydrochloric acid may also be collected in tubes over quicksilver, and its solubility in water and alkalis can then be studied.

EXERCISE B'. To detect chlorine in hydrochloric acid gas.

Proceed as in Exercise A', but place dry black oxide of manganese in *B* (Fig. 64, p. 194).

EXERCISE C'. To prepare chlorine.

Proceed as for making hydrochloric acid, but place in the generating flask damp black oxide of manganese, add hydrochloric acid to this and warm gently. Work at the fume closet.

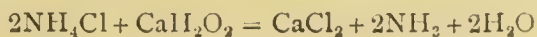


A mixture of common salt, black oxide of manganese and sulphuric acid may also be used.

Study the appearance of the solution obtained in *B*. Notice also its colour, smell, power of bleaching indigo, &c.

A little chlorine may be collected in jars by displacement of air, when it will be found on a trial that metals and hydrogen unite with it with avidity, but great care must be taken as chlorine is extremely dangerous, and has caused death when inhaled. Hence experiments with it may only be performed in a draught cupboard.

EXERCISE D'. 1. To prepare ammonia. Place in the generator *A*, Fig. 63, p. 192 (80), a mixture of sal-ammoniac and slaked lime with a little water and warm gently :



*L

Examine the colour, smell, action on litmus, &c. of the solution you obtain. Compare its action on solutions containing dilute acid, lead nitrate, ferric chloride, copper sulphate and on litmus with that of a dilute solution of soda (NaHO).

If you collect a jar of the gas by upward displacement of air, you can observe its behaviour when mixed with hydrochloric acid.

2. The preparation of nitric acid (see p. 269) should be done now if previously omitted.

3. Preparation of sulphur dioxide. This gas is evolved when many metals, e.g. copper, quicksilver or lead are heated with strong sulphuric acid. The apparatus used for making solution of hydrochloric acid may be employed. The student should prepare some of this gas and study its solubility in water, its action on litmus, its smell, colour, &c.

EXERCISE E'. 1. Prepare sodium oxide by heating a little sodium in a boat in a current of dry air. Observe whether this oxide is soluble and alkaline in solution like the hydroxide.

N.B. Take care that no sodium remains in the sodium oxide.

2. Prepare zinc oxide, ZnO , cupric oxide, CuO , and lead oxide, PbO :--

(a) By heating nitrates of these metals.

(b) By igniting their carbonates.

(c) By precipitating them as hydroxides, by means of soda, and heating the precipitates strongly.

3. Prepare cuprous oxide, Cu_2O , by warming a solution of copper sulphate, containing a little grape sugar, with alkali. Collect, wash and dry the precipitate.

Compare its appearance with that of cupric oxide.

Warm cupric and cuprous oxide separately with a little strong hydrochloric acid and observe the distinctive characters of the chlorides thus produced. Examine the effect of heating cuprous oxide in air.

4. Prepare peroxide of lead, PbO_2 .

(a) By digesting red lead, Pb_3O_4 , in dilute nitric acid, washing and drying the precipitate.

(b) By warming a solution containing a salt of lead with solution of sodium peroxide, or by warming a solution containing a salt of lead with large excess of bleaching solution.

Heat a little peroxide of lead, observe the qualities of the residue, say what it is, and ascertain the nature of the gas evolved.

5. Prepare a little tin dioxide.

(a) By digesting metallic tin in strong nitric acid; washing, drying, and igniting the precipitate.

(b) By adding alkali to a solution of stannic chloride, and heating the precipitate after washing it.

6. Prepare stannous oxide by adding sodium carbonate to a solution of stannous chloride, and boiling the precipitate with water containing a little free potash (KHO). Observe how these two oxides differ in appearance.

7. Prepare iron, copper and lead from their oxides by reducing them in a current of hydrogen or by coal gas, see Exp. 257, p. 391 (126) or by heating the oxide with carbon to a high temperature.

8. Prepare metallic lead, tin and copper by the method described on p. 391 (126) Exp. 258, and prove by experiment that zinc goes into solution in place of the metal removed.

9. Prepare quicksilver in the same way, using copper to displace it from a solution in nitric acid. Afterwards drive off the quicksilver from the copper by heat in a narrow glass tube.

10. Prepare specimens of nitrates and chlorides of any three of the following metals, sodium, zinc, copper, lead, tin, iron. Ascertain whether you can recover the acid from portions of these salts, (a) by the action of sulphuric acid on them, (b) by passing hydrogen sulphide through solutions to precipitate the metals as sulphide.

Ascertain whether you can obtain chlorine from one of these chlorides.

Observe the results of heating portions of the nitrates, chlorides and sulphides of the above metals strongly in hard glass tubes.—Lecture notes or *Inorganic Chemistry* may be consulted.

11. Ascertain whether salts of the above metals will give sulphides as precipitates with hydrogen sulphide, when the latter is passed through slightly acid solutions of them, and whether they give sulphides from solutions rendered alkaline by ammonia.

Prepare specimens of sulphide of zinc and of tin.

12. Prepare neutral specimens of the chloride, sulphate and nitrate of ammonium. Compare these salts with the sulphate and chloride of potassium, and study their behaviour when heated.

Do not attempt to neutralize the strongest solution of ammonia, but dilute it considerably with water before you add the acid to it.

EXERCISE F'. Ascertain as nearly as you can the proportions in which zinc, tin and lead replace the hydrogen of acids:—

1. Find the combining weight of zinc by dissolving a known mass of zinc in nitric acid in a small basin or large crucible, evaporating cautiously to dryness, igniting the residue till it ceases to lose weight and weighing the resulting oxide.

2. Obtain small sheets of zinc about one or two millimeters in thickness, weigh these, then immerse them separately in solutions containing tin chloride, and lead acetate, leaving them in the solutions until fairly thick deposits of tin and lead have formed upon them. Remove the crystalline crusts completely*, drain them, taking care not to lose any of the metal, dry them by strong pressure between sheets of bibulous paper in a vice and weigh the metal. Also weigh the residue of zinc in each case after cleaning and drying it. Then deduce the combining weights of zinc, lead and tin.

* You must not continue the immersion too long, nor dry the metal by means of heat or oxides will be formed.

EXERCISE G'. To find the composition of iron rust.

Heat a known mass of iron rust in a gentle current of hydrogen or coal gas as described in Exp. 74, p. 99 (63). Allow the reduced iron to cool thoroughly before you remove it from the current of hydrogen. Weigh the iron.

Calculate the composition of the iron rust and deduce the equivalent weight of iron from your result.

EXERCISE H'. To find the combining weight of carbon and the composition of carbon dioxide.

Place about half a gram of pure charcoal made by strongly igniting sugar in a porcelain boat and find their weight; place the boat at the end nearest *G* of a hard glass tube *E*, Fig. 32, p. 60 (52), previously filled for several inches towards *D* with black oxide of copper. Let *D* contain soda lime in fragments and let its weight be known. Heat the carbon strongly, passing dry air* slowly through the apparatus by way of *G*. When the carbon is consumed reweigh the boat with any residue it may contain, and also reweigh *D*.

Find the weight of carbon taken, the weight of carbon dioxide formed and calculate the amount of oxygen present in this dioxide.

State the combining weight of carbon as deduced from your results if that of oxygen be 8.

EXERCISE J'. To collect and weigh a precipitate.

In a former experiment a somewhat rough mode of separating soluble and insoluble substances was employed. It was open to the objection that two filter papers of equal diameter may not have exactly equal weights. The following method gives better results.

Get about 1 gram of pure silver nitrate, dissolve it in about 20 c.c. of distilled water in a beaker, and add solution of pure hydrochloric acid as long as it causes a precipitate. Allow this to settle for an hour or two in a warm place. Decant the clear liquid through a filter paper (one rendered free from ash by treatment with acids should be used). Pour water on the residue, mix by shaking gently, allow the precipitate to settle and decant the washings as before; repeating this process till the washings are quite free from acid. Then wash every particle of the silver chloride on to the filter. Allow it to drain, remove as much of the water as you can and dry it cautiously in an air bath. Carefully transfer as much as you can of the precipitate to a weighed crucible; fold the filter paper with the remaining adherent precipitate into a roll, wrap it loosely with a platinum wire and set the paper alight, holding it over the inverted lid of the crucible to catch any particles that may fall from it. Place the ash, which will contain some metallic silver, on the crucible lid, warm it gently, first, with a drop or two of nitric acid and then with a drop of hydrochloric acid to convert the silver into chloride. Finally carefully dry the lid of the crucible and also the chloride of silver by heating them, and reweigh the crucible and its contents.

* It may be necessary to substitute a current of oxygen, in order that the carbon shall burn.

This mode of procedure gives more accurate results than the former one. But its employment demands more skill and also more knowledge. Suppose, for example, you were to precipitate calcium as oxalate and heat the contents of the crucible moderately before weighing them; then you would have in the crucible not calcium oxalate but calcium carbonate. Whilst if the residue were very strongly heated it would consist of quicklime. Hence the properties of the precipitates must be well known if we are to employ this method with success.

EXERCISE K'. To find the composition of tin dioxide.

Place a gram or so of metallic tin in a rather large crucible of known weight inclined on a triangle as shown in Fig. 55 A.

Drop nitric acid on this, drop by drop, warming gently till the metal is destroyed. Warm the contents of the crucible cautiously to expel excess of nitric acid. Then heat the crucible and its contents strongly and weigh them.

Find the percentage of tin and oxygen in the oxide formed, and deduce the combining weight of tin if that of oxygen be 8.

EXERCISE L'. To find the composition of silver chloride.

1. Dissolve a known mass of metallic silver in a little nitric acid* slightly diluted in a dish or crucible. Then add slight excess of hydrochloric acid*. Evaporate cautiously to drive off excess of acid and heat the residue till it shows signs of melting at the edges. Then weigh it. From the composition of the chloride calculate the combining weight of silver if $\text{Cl} = 35.5$, or that of chlorine if $\text{Ag} = 108$.

To prevent loss of silver from spitting whilst it is dissolving it may be dissolved in a small flask inclined on its side. The contents of the flask being afterwards transferred to a dish or crucible with the usual precautions.

2. Add excess of hydrochloric acid to a solution containing a known weight of silver in nitric acid diluted with eight or ten times its volume of water. Collect the precipitate on a filter as described on p. 153 k, wash, drain, dry, weigh it and deduce the composition of the chloride as before.

3. Place a known mass of silver chloride in a boat of known weight in a glass tube as described in Exp. 53, p. 60 (52). Heat the chloride till it melts and convey a current of dry hydrogen or coal gas† through the tube. [Test the escaping gas for hydrogen chloride]. When the chloride is completely reduced weigh the residue of silver. Calculate the composition of the silver chloride as before.

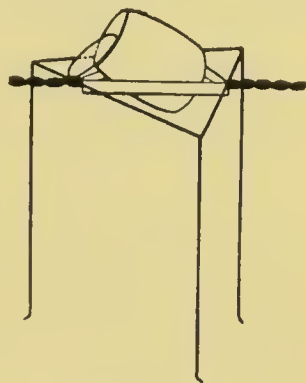


Fig. 55 A.

* These should leave no residue when evaporated to dryness.

† Coal gas contains a large proportion of hydrogen.

EXERCISE M'. To find the composition of marble (CaCO_3) or magnesite (MgCO_3).

Heat a known mass of one of these compounds in a crucible to bright redness till they cease to lose weight. From the mass of marble taken and the mass of carbon dioxide expelled find the proportions of lime, CaO , and carbonic acid gas (CO_2) in the marble.

EXERCISE N'. Find how much sodium sulphate (Na_2SO_4) you can obtain from 100 grams of sodium chloride.

Heat a known mass of pure salt, previously fused, cautiously with strong sulphuric acid. When no more hydrogen chloride is given off drive away excess of sulphuric acid by heat, cool and weigh the residue of sulphate.

Similar measurements may be made using potassium chloride or the carbonates or bicarbonates, or nitrates of sodium and potassium. The acid of the salt taken must of course be a volatile acid.

EXERCISE O'. To find the equivalent weight of sodium.

Weigh in a closed vessel a small clean block of sodium. Cut it up into very small pieces and dissolve these two or three at a time in a little alcohol. Dilute the solution, add slight excess of hydrochloric acid; evaporate to dryness and weigh the sodium chloride. From your result calculate the combining weight of sodium if that of chlorine is 35.2.

EXERCISE P'. Zinc may be dissolved in excess of hydrochloric acid and weighed as chloride. But it must be weighed very quickly as soon as it is cool, for it is hygroscopic in a high degree. Find the composition of zinc chloride in this way.

The best plan, perhaps, is to weigh the dish containing the chloride in the ordinary way. Then to reheat and weigh again. A second weighing can, of course, be made much more quickly than the first, and a third even more quickly than the second, since at a third weighing one knows very nearly what weights will be required, and these can be placed on the scale pan beforehand.

EXERCISE Q'. To find the amount of copper in a salt or solution containing that metal.

Add to a hot solution of the salt excess of solution of sodium hydroxide, boil, collect the black precipitate, CuO , as described in Exercise J'. Wash, dry, and weigh it.

EXERCISE R'. To measure the carbonic acid gas evolved by a carbonate when it is dissolved in an acid.

Obtain a little of the carbonate, for example some marble in small pieces, place a known weight in the bottle *A*, Fig. 55 B, with enough water to cover it. In *B* put rather more hydrochloric acid than is required to dissolve the carbonate taken. Fill *C* with calcium chloride, securing it in position by pads of asbestos or glass wool at *D D*. Close *E E'* by means of rubber caps plugged with small pieces of glass rod.

Weigh the apparatus with its contents. Pour the acid on the marble gradually after opening *E* so that the gas is given off in a not too rapid stream, that it may be dried well in *C*.

When all the marble is dissolved draw a current of air slowly through the flask to remove the carbonic acid gas and re-weigh the apparatus. From the weight of the carbonate taken and from that of the carbon dioxide lost deduce the percentage of lime, CaO , and carbonic acid gas CO_2 in the marble.

Other applications of this method consist in determining the hydrogen set free when a metal, e. g. zinc, is dissolved in an acid. Finding the proportion of a given carbonate in a mixture. Distinguishing carbonates from bicarbonates by ascertaining the amount of carbonic acid gas contained in them. See also Exp. 217, p. 320. Several of these cases should be studied by the student if time permits.

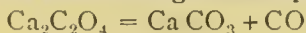
EXERCISE S'. To find the proportions of the volatile and non-volatile constituents of a substance.

1. Obtain a suitable mixture, for example, a mixture of iron rust and oxide of mercury. Weigh out a small quantity of it into a tared crucible. Drive off the constituents of the latter substance by heat and weigh the crucible and iron rust.

How can you make sure that no mercury oxide remains?

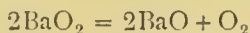
2. Determine the loss of weight when ammonium and magnesium phosphate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is heated to redness, and ascertain whether the residue consists of $\text{Mg}_2\text{P}_2\text{O}_7$.

Heat a known weight of calcium oxalate in a covered crucible and weigh the residue. Ascertain if the loss of weight corresponds to the equation—



Ascertain if the residue really is calcium carbonate by suitable tests.

Ascertain the proportions of BaO_2 in a sample by finding its loss of weight when heated strongly:—



Similar investigations may be made:—

1. With finely powdered barium oxalate, $\text{BaC}_2\text{O}_4 = \text{BaCO}_3 + \text{CO}?$

2. Lead peroxide, $2\text{PbO}_2 = 2\text{PbO} + \text{O}_2?$

EXERCISE T'. To separate and measure the alcohol in such a solution as beer or wine. Obtain about 300 or 400 c.c. of beer, which should be filtered and then carefully measured. Distil the beer, using a flask and a Liebig's condenser, gently till about one-third remains in the retort; ascertain whether what now distils is pure water. If so, make up the distillate to the

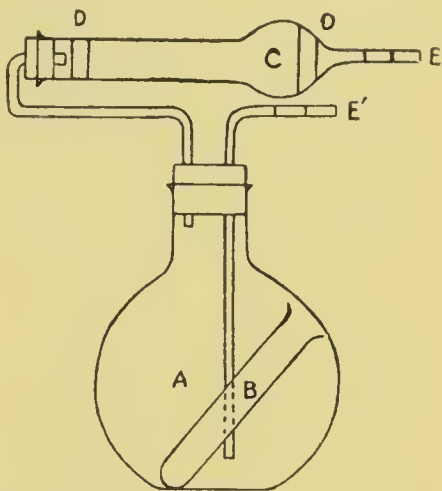


Fig. 55 B.

volume of the beer taken by adding water. Then find its density, constructing a curve if necessary by the aid of the following table :—

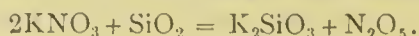
<i>Per cent. of alcohol.</i>	<i>Specific gravity at 15.5° C.</i>
0	1.0000
1	0.9981
2	0.9963
3	0.9944
4	0.9928
5	0.9912
6	0.9896
7	0.9880
8	0.9866
9	0.9852
10	0.9839
11	0.9826
12	0.9813

EXERCISE U'. To measure the constituents of a sample of sodium bicarbonate.

Place a weighed quantity of the salt in a boat in a hard glass tube, connect one end of the tube with a U tube containing strong sulphuric acid on pumice stone, and join to this a second U tube containing strong solution of potash on pumice, or soda-lime. Close the end of the tube containing the bicarbonate, and gradually raise its temperature so that a steady, but not too rapid, stream of gas is evolved. When no more gas escapes draw a stream of air through your apparatus to remove every trace of water and carbonic acid gas from the vessel containing the residue of sodium carbonate. Then from the gain of weight of the U tubes, and from the weight of the soda left in the boat, deduce the proportions of water, carbonic acid gas and soda, Na_2CO_3 . Check your results to make quite sure nothing has been lost.

Before commencing such an experiment as the above, you should draw a diagram of the apparatus you propose to use, and when you think your design is correct show it to your master before you construct it.

EXERCISE V'. Ascertain whether it is true that nitrates are decomposed by heating with silica according to the reaction



Prepare some pure and dry nitre by fusing a little of the salt (use the lowest temperature that will effect your purpose) in a porcelain dish. Powder the fused salt whilst still warm after pouring it in a molten state on to a plate, add about half a gram of the powder to about two grams of finely powdered silica, previously ignited in a crucible to dry it, cooled and weighed, mix well by means of a rod weighed with the crucible. Heat the mixture to a low red heat

for half an hour, cool in a desiccator and weigh, reheating and reweighing till it no longer loses weight.

EXERCISE W'. To find the amount of silver in a solution containing free acid. In the process described on p. 153 *e*, potassium chromate was used as an indicator. This cannot be done if a strong acid is present, as silver chromate is soluble in acids. In such a case the best mode of proceeding is to add to the acid silver solution at once almost enough solution of the chloride to complete its precipitation, and then to shake very vigorously. When this is done all the precipitate will subside, leaving a clear solution. Then add more solution of the chloride. This will cause further turbidity which can be removed, as before, by violent shaking. By proceeding very cautiously in this way you will succeed in ascertaining the point at which adding solution of the chloride has no further effect.

EXERCISE X'. To measure the ammonia in a compound such as iron and ammonium sulphate, or in a mixture of salts containing ammonium. Obtain a glass flask of about 250 c.c. capacity, attach a separator (B, Fig. 68) and a delivery tube to it by an indiarubber cork. The end of the tube of the separator should nearly reach the bottom of the flask. Place the salt, say 1 gram, in the flask with about 50 c.c. of water and fill the separator B with strong solution of soda. Connect the delivery tube with a suitable vessel containing 100 c.c. of normal acid. Heat the contents of the flask, and drop in the soda very gradually to expel the ammonia. Finally boil the contents of the flask to expel the last traces of ammonia. Then make up the acid solution of ammonia thus obtained to some convenient volume, say to 300 c.c., and titrate portions with standard alkali. A convenient absorption apparatus may be made, using a rather smaller flask, like *A E* in Fig. 68, but replacing the separator by a 50 c.c. pipette, the tip of which should just dip into the liquid in the flask. It must be provided with a *U* tube *E* containing broken glass made wet with part of the standard acid employed to absorb the ammonia. The contents of this *U* tube must, of course, be carefully washed into the flask before the residual acid is titrated with alkali.

PART III

THE CHIEF NON-METALS AND THEIR PRINCIPAL
COMPOUNDS

CHAPTER XI

OXYGEN (O_2): Atomic weight, 15.88. OZONE (O_3)

WE have already learnt that oxygen is a colourless, odourless, tasteless gas, only slightly soluble in water, which occurs in the air, in water, in most of the rocks, and forms compounds with all other elements, except fluorine, bromine, and the gases, argon, neon, &c., lately discovered in the air. Also that it was first obtained by Priestley, in 1774, by the action of heat on oxide of mercury; that it supports combustion; that many of its compounds with the non-metals form acids when dissolved in water, and that its compounds with the metals are many of them basic. We have also learnt that oxygen plays a most important rôle in the life processes of plants and animals.

117. Methods of making oxygen. Oxygen is no longer prepared by heating mercuric oxide. It is usually obtained either from chlorate of potassium ($KClO_3$) (151), or from atmospheric air.

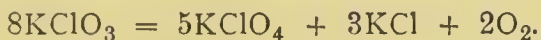
1. Heat some chlorate of potassium, previously mixed with about one-tenth of its weight of black oxide of manganese (MnO_2), in a small flask made of hard glass, or better in a copper tube or retort, provided with a delivery tube, and collect the gas over water. The change which occurs may be represented as follows:—



Oxygen made in this manner usually contains traces of chlorine, which may be recognized by its smell.

The action of the black oxide of manganese is said to be *catalytic*; the oxide remains practically unaltered at the end of the experiment, and might be used again. We do not very well understand how it acts, but its presence undoubtedly causes the oxygen to separate at a lower temperature than is required to decompose chlorate of potassium alone.

If oxygen be needed in a pure state, the chlorate of potassium must be heated alone. The chlorate is understood to decompose in two stages: at the first stage only part of the oxygen is liberated, a salt called potassium perchlorate (KClO_4) being formed. The following equation is said to represent the change, but the exact proportion of oxygen set free depends to a certain extent on the temperature employed:—



If the salt is more strongly heated the perchlorate is also decomposed:—



A little potash is sometimes added to the chlorate in order to ensure the complete absence of chlorine from the oxygen.

The student will do well to compare the colourless salt, left after chlorate of potassium has been strongly heated, with some of the original salt. He will find that a solution of the ignited salt gives a copious precipitate with a solution of silver nitrate, owing to the forming of insoluble silver chloride (AgCl), whilst the chlorate gives no such precipitate if it be pure; and also that if *very small* fragments of each be touched separately with a drop of strong sulphuric acid they behave quite differently. The colourless salt in question is chloride of potassium (KCl) (see equations above).

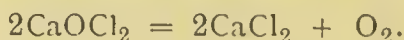
2. The manufacture of oxygen from the air—Brin's process.

It has long been known that when oxide of barium (BaO) is moderately heated in atmospheric air it forms barium dioxide (BaO_2), but that at a higher temperature the dioxide is resolved again into baryta (BaO) and oxygen. This fact has of late years been taken advantage of by the manufacturers of oxygen.

A current of air is forced through purifiers containing lime and soda into retorts containing the baryta heated to low redness. When the baryta is sufficiently charged with oxygen, the supply of air is discontinued, and the retorts are exhausted by air-pumps; as soon as the pressure has fallen about 650 mm. below that of the atmosphere, the barium peroxide begins to give off oxygen. This is withdrawn by the pumps and delivered into gas-holders, where it is stored ready to be compressed in the steel cylinders in which it is distributed. The same baryta can be used, it is said, for many months, or even for years, if it be occasionally broken up.

3. Oxygen from bleaching powder. Place some bleaching powder (150), mixed to a thin paste with water, in a flask fitted with

a delivery tube, pour a thin layer of paraffin over it to prevent frothing, add a few drops of cobaltic chloride *, and heat the mixture gently on a sand bath. A considerable volume of oxygen will be evolved, which may be collected in the usual manner, whilst a solution of calcium chloride will be left in the flask :—



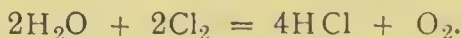
If solution of bleaching powder be heated without the oxide but little oxygen will be evolved. The mode of action of the oxide of cobalt is not really understood; but it would seem to afford us a fresh example of *induced action* or *catalysis* (see 1 above). It has been suggested that a higher oxide of cobalt may be formed, and at once split up into free oxygen and the original oxide; in short, that the latter may act as a sort of oxygen carrier.

Oxygen may also be generated in a variety of other ways.

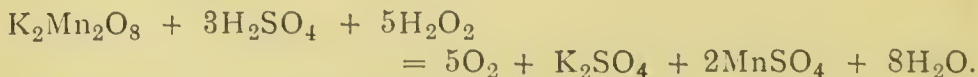
4. By the electrolysis of acidulated water (39).

5. By heating the oxide of silver (Ag_2O), or gold (Au_2O_3), or by heating the black oxide of manganese to redness; in the latter case the red oxide of manganese (Mn_3O_4) is left.

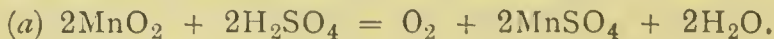
6. By the action of chlorine on water at a red heat. The chlorine mixed with steam may be passed through a red-hot tube provided with a delivery tube :—



7. By acidulating some solution of hydrogen peroxide with sulphuric acid, placing the mixture in a flask provided with a thistle funnel and a delivery tube, and adding solution of potassium permanganate ($\text{K}_2\text{Mn}_2\text{O}_8$)† slowly through the thistle funnel, and collecting the gas which is liberated :—



8. By acting with sulphuric acid on certain peroxides, or on certain salts which are rich in oxygen; for example :—



* The alkali in the bleaching powder, together with the salt of cobalt, yield oxide of cobalt. The oxides of copper, nickel, and iron are said to act similarly.

† Here we have an example of two powerful oxidizers mutually acting as reducing agents (see also ozone, 124).

‡ In the presence of sufficient water chrome alum would be formed (see 482).

118. Some properties of oxygen. Though oxygen is colourless in small quantities, it appears bluish when light is transmitted through a column of the strongly compressed gas, and liquid oxygen, which boils at about -183 , also has a bluish tint. Its density is 15.9. It can be liquefied at temperatures below -118.8° under a pressure of 51 atmospheres (see critical temperature and critical pressure, 130); it has been solidified and is attracted by a magnet. A litre of water will dissolve about 40 c.c. of oxygen at 0° , and under a pressure of 760 mm., and it is six times as soluble in alcohol. It is absorbed or *occluded* by molten silver, from which it escapes when the metal solidifies (545), and also by finely divided platinum.

Oxygen is one of the most electro-negative elements (Expt. 79); it enters into direct combination with almost all other elements except the halogens, gold, platinum, argon, and the other recently discovered constituents of the atmosphere.

In the liquid state, probably owing to its low temperature, oxygen is chemically indifferent—potassium, sodium, and even phosphorus may be plunged into liquid oxygen without combination taking place. On the other hand, it is found that finely divided iron, or lead, when freshly reduced, ignites spontaneously in air or oxygen at ordinary temperatures.

In many cases it would seem that oxidation can only occur in the presence of at least a trace of moisture. Thus phosphorus, sulphur, and carbon refuse to burn in carefully dried oxygen.

EXPERIMENT 94. To observe the behaviour of phosphorus or sulphur in dried oxygen. Draw out one end *D* of a piece of combustion tube, about 40 centimetres in length, before the blow-pipe. When the glass is cool, introduce some sulphur or a little phosphorus sealed up in glass bulb *A* then place a plug of glass wool

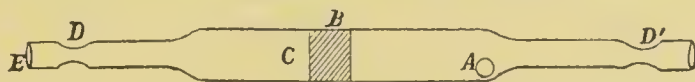


Fig. 56.

at *B*, and some phosphoric anhydride at *C*. Draw out the ends *D* and *D'* as in the figure, pass a current of oxygen through the tube from *E*, and, when the air is displaced, seal the tube at *D* and *D'* before the blow-pipe. Break *A* by shaking the tube, and allow the contents of the tube to dry for six months. At the expiration of that time you

will find that the sulphur or phosphorus may be distilled within the tube, but that they will not catch fire.

Several other chemical changes are similarly dependent on the presence of moisture; for example, dry carbon monoxide will not explode with dry oxygen and, as we shall presently see, completely dried chlorine does not combine with some metals, though it does do so with others.

119. The part played by oxygen in respiration. See 77.

120. The general properties and classification of oxides.

It was shown by Experiment 77 that whilst oxides of non-metals are often acidic, many metallic oxides are basic. But the oxides do not all fall into these two classes.

EXPERIMENT 95. To study the behaviour of two oxides of lead with hydrochloric acid. Heat 8 or 10 grams of well dried and powdered litharge in a hard glass tube *E* (Fig. 32). Pass hydrochloric acid, generated from salt and sulphuric acid and dried by oil of vitriol in *D*, over this oxide, and let the escaping gas and vapour pass through a well cooled U tube *G*.

Then examine the contents of *E* and *G* as described below:—

1. Heat the contents of *E* with some boiling water, decant the solution into a dish, and treat the undissolved portion with more hot water; mix the solutions thus obtained and allow them to cool; collect the crystals which form on a filter, wash them with a *little cold* water, drain and dry them.

(a) Examine their behaviour with litmus, and ascertain whether they neutralize either acid or alkali.

(b) Heat a few of the crystals before the blow-pipe with cyanide of potassium on charcoal. You will obtain globules of a soft metal which mark paper, and generally resemble lead.

(c) Warm another portion of the crystals with strong sulphuric acid and manganese dioxide. A greenish-yellow gas resembling chlorine (see 136) will be evolved.

From these results it is evident that hydrochloric acid and lead oxide yield a neutral compound of lead and chlorine. This is lead chloride (PbCl_2).

2. The contents of *G* will be liquid, nearly colourless, and very acid. They will probably fume strongly in the air, and also when brought near ammonia gas. They will give a blue colour to dry cupric

sulphate, and exhibit all the properties of a solution of hydrochloric acid in water (143), showing us that lead oxide and hydrochloric acid yield lead chloride and water. No other product has ever been obtained by the action of these two compounds, and we represent the change as follows:—



3. Now make a similar series of experiments, using the puce-coloured oxide of lead in place of litharge. You will again obtain a white solid which has the properties and composition of lead chloride; but the liquid collected in *G* in this case will contain free chlorine as well as water and excess of hydrochloric acid.

EXPERIMENT 96. **The action of the two oxides of lead with strong sulphuric acid.** Heat a little litharge and some puce oxide of lead with strong sulphuric acid in separate test tubes, closing the mouths of the test tubes loosely with the thumb, or by means of watch glasses; after a little while test the gas in the upper parts of the tubes with glowing splinters of wood. You will find (*a*) that litharge is converted into a very insoluble white salt (this is lead sulphate), and that no oxygen is evolved; (*b*) that the puce oxide of lead forms a similar white solid, and that it gives off oxygen.

If ferric oxide or iron rust, calcium oxide or lime, magnesia, baryta, oxide of zinc, black oxide of manganese and red lead are similarly treated with hydrochloric acid, it will be found that they all resemble either litharge or puce oxide of lead. Most of them will simply neutralize the acid, but two [which?] will exhibit oxidizing power, liberating chlorine. Thus the metallic oxides may be divided into two classes:—

1. Those which neutralize acids, forming salts and water. These are termed *basic oxides*.

2. Those which form salts with acids, but which also evolve oxygen, or yield an oxidation product such as chlorine. These may be termed *basic peroxides*.

When the same metal forms a basic oxide and also a basic peroxide, it will be found that the latter contains a greater proportion of oxygen than the former. Thus the composition of litharge is expressed by the formula PbO , whilst the formula of the puce oxide of lead is PbO_2 . Again, whilst baryta (BaO) is a basic oxide, the higher oxide with the formula BaO_2 is a peroxide. Recently a few salts corresponding to the peroxides have been discovered: one of these is the tetrachloride of lead (PbCl_4), another the tetra-acetate of the same metal.

EXPERIMENT 97. The properties of chromic anhydride. Acidic peroxides. Prepare a few crystals of chromic anhydride (483); heat separate portions of them with a solution of hydrochloric acid, with strong sulphuric acid, and with a solution of an alkali. You will find that this oxide yields chlorine with hydrochloric acid, losing its orange colour, and giving a green solution; that it yields oxygen when warmed with strong sulphuric acid, again giving a green solution*. When solution of soda is added to the anhydride, its colour becomes pale yellow, and, if care be taken, a neutral, or nearly neutral, solution is obtained, which yields pale yellow crystals of sodium chromate when it is concentrated. A dilute solution of chromic anhydride in water liberates carbon dioxide from an alkaline carbonate.

An oxide, like chromic anhydride, which possesses marked power as an oxidizer and yields an acid when dissolved in water, may be termed an *acid peroxide*. The acid peroxide of a given metal, like the basic peroxide, always contains a greater proportion of oxygen than the basic oxides of the same metal. Thus the formula of the chief basic oxide of chromium is Cr_2O_3 , and that of the acid peroxide is CrO_3 .

Thus, besides the acidic and basic oxides mentioned in 109, there are also acidic peroxides and basic peroxides, and to these we may perhaps add a fifth class, the members of which, like water and carbonic oxide, do not exhibit the characteristic qualities of either the basic oxides, the acidic oxides, or of the peroxides.

Just as it is not possible to distinguish sharply between other classes of substances—just as we cannot clearly classify every element as a metal or as a non-metal—so it is not always possible to classify the oxides, for some oxides which are distinctly acidic to strong bases are not altogether unlike basic oxides in their behaviour with strong acids (see 410 and 429). It is desirable that the student should be made aware of this at once, but a fuller consideration of the matter must be postponed.

121. Detection of oxygen. Oxygen may be distinguished from the other colourless gases by its power of supporting the combustion of carbon and its compounds; by the characters of the oxides; by its producing water and nothing else when it is exploded with

* These green solutions are believed to contain salts of chromium, but you cannot obtain the salts in the crystalline state by evaporating the solutions, except after some delay.

hydrogen ; and by forming a red gas (NO_2 or N_2O_4) when mixed with nitric oxide (NO) (239).

Oxygen may be separated from other gases by means of an alkaline solution of pyrogallic acid (Expt. 62).

122. Why oxygen is considered an element. 1. Oxygen has never been split up into more simple substances by the action of such agents as electric discharge or high temperature.

2. When oxygen combines with other elements, it behaves like a simple substance, not like a complex substance. The meaning of this statement will be best conveyed by an example.

We have seen that when hydrogen is exploded with excess of oxygen, water is formed, and no one has ever detected any other product. Now if some marsh gas were similarly treated, water would be formed as in the case of hydrogen, but the water would be accompanied by some carbon dioxide (CO_2). Thus, whilst we can obtain only one substance by oxidizing hydrogen, we can obtain two substances by oxidizing marsh gas. Hydrogen, in short, behaves like a simple substance when it is oxidized, marsh gas like one that is more complex.

Now when oxygen is made to act with such substances as carbon, phosphorus, and magnesium, it behaves like hydrogen and not like marsh gas. From carbon and oxygen we get carbon dioxide and nothing else ; from phosphorus only phosphoric oxide (257) ; and from magnesium only magnesium oxide.

It is true that if too little oxygen be used we may get from carbon, for example, a second substance ; but this does not differ from carbon dioxide, as water does ; it is simply a lower oxide of carbon which, if supplied with more oxygen, is very readily converted into the dioxide.

Oxygen, then, is regarded as an element, because it has never yet been decomposed by any physical process ; and because when it unites with other elements it either produces a single oxide, or two or more oxides, which can be changed the one into the other by adding or subtracting oxygen.

123. The atomic weight of oxygen. Analyses of water have shown that the equivalent weight of oxygen is not far from 7.95. But the smallest quantity of oxygen which has ever been found in a molecular proportion of any volatile compound containing it is

twice as great as this ; therefore we may adopt the value 15.9 for its atomic weight.

As the equivalent weights of the elements are more frequently deduced from the composition of their oxides than from that of their hydrides, it has been proposed that oxygen should be adopted as the standard of comparison, and that 8 should be taken as its equivalent weight. The equivalent weight of hydrogen would then be 1.01.

124. An allotropic form of oxygen—Ozone (O_3). We now, for the first time, meet with a chemical change in which an element is transformed into a new substance, but still remains an element, for nothing is added to it in the change. Such substances are called the allotropic forms, or allotropes of the original elements.

The power of undergoing changes of this sort is not, it may be mentioned, confined to the elements ; compounds sometimes undergo similar transformations.

EXPERIMENT 98. To ozonize air by means of phosphorus. Place a stick of phosphorus in a glass cylinder with one end partly immersed in water. Boil a pinch of starch with a few cubic centimetres of water, and add to the solution a crystal of iodide of potassium. Then expose strips of filter-paper, moistened with this solution, to atmospheric air, and also to the air in the cylinder containing the phosphorus. The former will probably remain unaffected for some time, but the latter will be turned blue. Notice also that the air which has been exposed to the phosphorus acquires a peculiar odour.

The odorous gas which thus acts on iodide of potassium and starch is called *Ozone*. It was first observed in 1785 by van Marum, whose attention was drawn to its existence by the odour which may be noticed when an electrical machine is in action.

EXPERIMENT 99. The preparation of ozone. Ozonized oxygen may also be obtained by the electrolysis of water (electrodes made of fine platinum wires should be employed), and by the action of sulphuric acid on barium dioxide, but it is most conveniently prepared by the action of the so-called silent discharge of electricity on oxygen.

A thin glass tube *A* (Fig. 57) is sealed before the blow-pipe, or cemented with paraffin wax into a slightly larger tube *B*, also of very thin glass and provided with two smaller tubes *C* and *H*. This instrument is placed in a cylinder *E*, containing acidulated water, and *A* is filled with the same liquid. Platinum wires *W W*, connected with the terminals of an electrical machine, are immersed in *A*

and *E*. The electrical machine is set in action, and oxygen is passed slowly through the annular space between *A* and *B*. When this is done, the oxygen which issues from *H* exhibits the odour and reactions of ozone. If *E* and *A* are cooled by ice, and if the oxygen is passed through the apparatus slowly, the issuing gas may contain as much as five or six per cent. of ozone.

EXPERIMENT 100. The properties of ozone. 1. Pass ozonized oxygen through a piece of india-rubber tube connected to *H*; the india-rubber will quickly fall into decay owing to the oxidizing power of ozone, and it is therefore necessary to employ paraffin joints for experiments with ozone. To fix a delivery tube to *H* slip a larger piece of tube *K* over the end of *H*, taking care that it fits rather closely, warm the tubes at the junction, and touch them at *H* with a lump of paraffin. The paraffin will melt, run between the glass surfaces, and when cool will form a satisfactory joint.

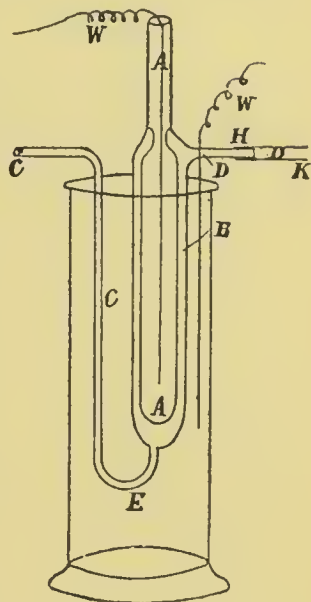


Fig. 57.

2. Place some clean quicksilver in a small clean flask, replace the air in the flask by ozonized oxygen, and then roll the mercury gently over the surface of the glass. It will adhere, forming a mirror. If you afterwards shake the mercury vigorously in the ozonized air, a dirty-looking grey powder will form. This consists of an oxide of mercury, and its formation illustrates very well the oxidizing power of ozone.

3. Pass ozonized oxygen through some very dilute solution of indigo. The colour of the indigo will disappear.

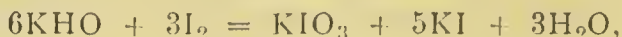
4. Expose some copper sulphide (CuS) on the surface of filter-paper * to ozonized oxygen. The black colour of the sulphide will disappear gradually as it becomes oxidized to copper sulphate (CuSO_4). Some other sulphides are similarly affected.

5. Pass ozonized oxygen into a solution of potassium iodide (KI). Iodine will be liberated, and may be recognized by the brown colour of its solution :—



* First dip the paper in a very dilute solution of a salt of copper, then expose it to hydrogen sulphide.

The proportion of ozone in ozonized oxygen may be measured by taking advantage of this reaction, but as iodine (I_2) reacts with potash (KHO), forming a mixture iodate and iodide :—



it is necessary to acidulate the product, in order to liberate the iodine before titrating the solution (205, 4).

This last reaction can only be used for detecting or measuring ozone in the absence of other oxidizing agents, as several of these liberate iodine from its salts (see Expts. 112, 126, 176).

6. Heat a short length of the delivery tube at *K* strongly, by placing the flame of a gas-burner beneath it, and repeat the previous experiments. You will now find that the issuing gas is inactive, for ozone is quickly destroyed by a temperature of 250° – 300° .

Ozone decomposes spontaneously at ordinary temperatures, so that ozonized oxygen gradually loses its charge. The rate at which the ozone disappears is rapid at first, but continues at a diminishing pace, and traces of ozone may be recognized after several weeks' exposure to a summer temperature. If the mixed gases have been very carefully dried, this spontaneous decomposition takes place more rapidly than when water is present. We have therefore in the change :—



an example of chemical change which is retarded by the presence of moisture.

Ozone is destroyed by contact with metallic silver, the silver usually being oxidized, and also by instable oxides (132).

If oxygen well charged with ozone be passed into a tube about two metres in length and provided with plain glass ends, the contents of the tube appear to be of a pale indigo blue colour when they are examined by transmitted light. Liquid ozone, which is readily obtained at -181.4° , but which is very explosive, has a deep blue colour.

A substance resembling ozone in its reactions may be observed sometimes in the neighbourhood of flames, and ozone has been produced, mixed with water, by plunging a jet of burning hydrogen in liquid oxygen.

Ozone is believed to be present in country air and to contribute to its healthfulness, and there is reason to hope that it may, in the future, prove valuable in the arts and in medicine.

Why ozone is considered to be an allotropic form of oxygen.

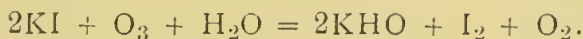
The formula of ozone. It was at one time supposed that ozone might contain hydrogen; but it has been repeatedly shown that it can be produced by the action of the electric discharge on highly purified oxygen.

When oxygen is ozonized, the volume of the gas concerned undergoes a very notable contraction. This fact, and the behaviour of the substance with certain reagents, led Dr. Odling to suggest, in 1861, that each molecule of ozone might not improbably consist of three atoms of oxygen, and be formed according to the following equation:—



According to this view, three volumes of oxygen should yield two volumes of ozone (see Avogadro's hypothesis, 91).

When ozone is allowed to act upon iodide of potassium the ozone disappears, and yet there is no decrease in the volume of the gas. This singular phenomenon becomes intelligible if we accept Dr. Odling's formula; because, as may be seen from the following equation, a molecule of ozone (O_3) could give up an atom of oxygen to the iodide and at the same time liberate a molecule of oxygen (O_2), which would occupy the same volume as the original molecule of ozone (Avog. hyp.):—



Dr. Odling's hypothesis is also supported by what is known concerning the rate of diffusion of ozone, which has been compared with that of chlorine ($D = 35.5$), and with that of carbon dioxide ($D = 22$), and has been found to approximate to that of a gas having the density 24 and therefore the molecular weight 48 (see 129). Further confirmation of Dr. Odling's views is to be found in the fact, first ascertained by Soret, that when measured volumes of ozonized oxygen are treated with turpentine (in which ozone appears to dissolve) on the one hand, and heated to destroy the ozone on the other, the results show that three volumes of oxygen are required to produce two volumes of ozone. The following modification of Soret's beautiful experiment will make this point intelligible.

EXPERIMENT 101. To find the composition of ozone (Fig. 58). *A A'* are two tubes of very thin glass, sealed together before the blow-pipe at *C*. *B* is a manometer dipping in strong sulphuric acid in *G*, and attached to the rest of the apparatus by means of a liquid joint at *D*. The outer vessel, *K*, and *A'* are filled with slightly acidulated ice-cold water. *E* is a small bulb of india-rubber filled with turpen-

tine. *E* having been removed, oxygen is passed through the apparatus from *F*. When the air is replaced by oxygen *T* is closed, after adjusting the liquid in *B* at a convenient level, and *E* is refixed to *F*. When all is ready the oxygen is submitted to the action of the

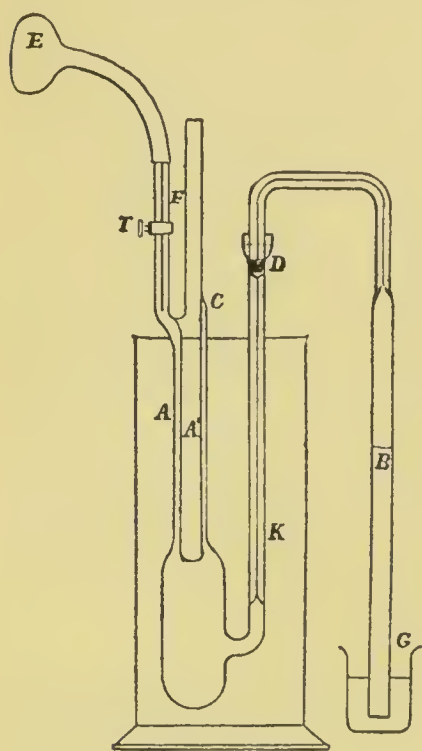


Fig. 58.

silent discharge, and when a sufficient contraction has taken place its amount is measured on a scale placed behind *B*. *T* is then opened, a little of the turpentine is squeezed into the ozone generator*, and the further contraction which then occurs is measured.

The results of these two operations show that whilst only two volumes of ozone are absorbed by turpentine, three volumes of oxygen have disappeared at the end of the experiment. Therefore, if turpentine absorbs ozone completely, it follows that three volumes, or molecules, of oxygen must go to the making of two volumes, or molecules, of ozone, as indicated by the above equation.

The exact nature of the change by which ozone is produced is not understood. We do not know

whether the discharge condenses the oxygen directly, or whether the sparks resolve the molecules into atoms which afterwards recombine to form larger groups. But, as ozone is so readily decomposed by heat, the latter hypothesis seems to be the more acceptable, for it is difficult to believe that ozone can be formed at the temperature of an electric spark.

For the oxidizing action of ozone see 124 and 132.

CHAPTER XII

HYDROGEN (H_2): Atomic weight, 1

WE have already learnt that hydrogen is a very light, colourless, tasteless, inflammable gas, which produces water and nothing else

* No error is caused by this operation as the bulb recovers its volume.

when it is burnt, which is present in all acids, and which may be obtained (Expt. 40) by dissolving zinc or iron in dilute sulphuric or hydrochloric acid. It was described by Cavendish, in 1766, but is supposed to have been first observed in the sixteenth century. It is less soluble in water than oxygen, and is the lightest gas known.

Hydrogen occurs, as you have already learnt, in water, and is a necessary constituent of the tissues of plants and animals.

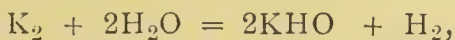
125. Modes of preparing hydrogen. 1. By dissolving zinc or iron in diluted sulphuric, or hydrochloric acid (Expt. 40). If zinc and sulphuric acid be used, the reaction may be written as follows (see also 411) :—



Owing to its lightness we can not only collect hydrogen over water in the pneumatic trough, or over quicksilver, but also by the upward displacement of air, that is, by inverting a cylinder *B* over the delivery tube *A*, as in Fig. 59.

2. Hydrogen may be made by the action of several metals on water.

(a) For the action of sodium and potassium, see Experiment 50. The following reactions occur :—



(b) For the action of iron on steam, see Experiment 52. The reaction which occurs is as follows :—



The magnetic oxide of iron (Fe_3O_4) is also formed in the blacksmith's shop, when the smith cools red-hot iron by plunging it in water.

(c) Zinc also decomposes hot water, especially if it be used in the form of a 'couple' made by coating zinc with copper.

Cover some clean granulated zinc in a flask with a solution containing 5 per cent. of copper sulphate. When the blue colour of the solution has disappeared, decant the liquid, pour some more of the solution of copper sulphate upon the metal and again decant the decoloured

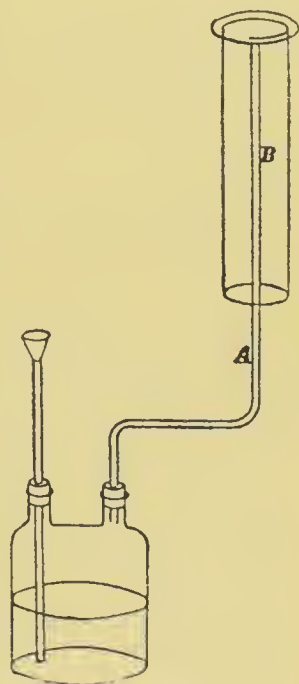


Fig. 59.

liquid. If now the zinc, with its coat of copper, be covered with warm water, the zinc will be oxidized, and hydrogen liberated.

(d) Hydrogen made by the action of zinc or iron on an acid is apt to be contaminated with compounds of arsenic and sulphur, or with certain hydrocarbons. Therefore, when pure hydrogen is required, magnesium may be employed with the purest acid obtainable.

The following reactions are sometimes employed for making hydrogen :—

(e) Aluminium or zinc is gently warmed with a solution of potash or soda.

This reaction is sometimes used for reducing nitrates to ammonia. Place a crystal of nitre in some solution of soda, and when it is dissolved warm a piece of aluminium foil in the solution ; after a time ammonia will be present in sufficiently large amount to be recognized by its smell.

(f) The electrolysis of acidulated water.

(g) The action of sodium, or potassium, on alcohol (spirit of wine) :



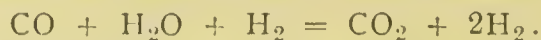
(h) Steam heated to the temperature of the electric discharge by means of sparks from a powerful electric machine yields small quantities of oxygen and hydrogen.

(j) Hydrogen, mixed with carbon monoxide (CO), is used on the large scale as a source of heat under the name of *water gas*. This mixture may be made by passing steam over coal or charcoal at a high temperature.

On the small scale the apparatus used for Experiment 52 may be employed :—



If the mixture of carbon monoxide and hydrogen, with excess of steam, be passed over red-hot bricks, carbon dioxide is formed :—



The carbon dioxide can then be removed by alkali, leaving the hydrogen.

126. Properties of hydrogen. Professor Dewar has condensed hydrogen to a liquid which boils at -252° to -253° ; this freezes to a non-metallic solid which melts at -257° to -256° ; by its evaporation *in vacuo* Professor Dewar has obtained the extremely low temperature of -260° (Olzevsky had previously obtained -225° by means of solid

nitrogen). Professor Dewar finds that the electrical resistances of the metals are very greatly reduced at these low temperatures, that of copper cooled in liquid hydrogen being only $\frac{1}{108}$ as great as at 0° ; he finds that the critical temperature of hydrogen is -238° to -240° , and its critical pressure 15.3 atmospheres*.

One litre of hydrogen at 0° , and under a pressure of 760 mm., weighs 0.0899† gram, and it is 14.5 times as light as air.

The low density of hydrogen may be elegantly demonstrated by hanging a good-sized beaker mouth downwards on one of the arms of a balance, placing the weights necessary to counterpoise it in the opposite pan, and delivering a gentle stream of hydrogen into its mouth. When this is done, the equilibrium of the balance is at once disturbed. The presence of hydrogen in the beaker may be proved afterwards by bringing a light to its mouth.

Hydrogen suffocates animals if it be impure, but pure hydrogen has been inhaled without injury when mixed with air. It burns with a non-luminous flame at atmospheric pressure, but under greater pressures its flame becomes luminous (74, 3).

If hydrogen and air, or oxygen, be mixed in suitable proportions and exposed to a flame, or an electric spark, a violent explosion occurs under ordinary pressure, which may be made less violent, or prevented, by rarefying the gases. It has been found that non-explosive combination can take place at moderate temperatures. Although some hydrides of the metals are known, the chief compounds of hydrogen are those in which it is associated with the non-metallic elements.

Hydrogen has never been decomposed by the action of heat or electricity; and the products of its interactions with the other elements give no evidence that it is a compound substance. When it is exploded with oxygen, for example, a single compound, water, results, not two compounds as in the case of marsh gas (see 122). In the absence, therefore, of any evidence that hydrogen is a compound substance, it is classed among the elements.

127. Is hydrogen a metal or a non-metal? Hydrogen has none of the physical properties which we associate with our conception of a typical metal (see 109 and 126). On the other hand, its chief oxide is not acidic like those of sulphur, phosphorus, and carbon, for water is

* Private communication.

† This is called the 'crith'; it is useful in calculations since the density of any gas multiplied by .0899 gives us the weight of a litre of that gas.

a neutral substance, though hydrogen peroxide (H_2O_2) is said to be acid to litmus. Hydrogen appears at the negative electrode when dilute acids are electrolyzed, just as the metals do when solutions of their salts are similarly treated, and, as we have seen, acidic hydrogen is readily replaced by metals. These facts seem to imply a similarity of function between hydrogen and the metals; but at the same time it must be mentioned that the hydrogen of many carbon compounds can be replaced by the non-metallic elements chlorine, bromine, and iodine. Therefore it would seem that hydrogen occupies an intermediate position among the elements.

128. The oxy-hydrogen flame, and oxy-gas flame. If we supply the air jet of a blow-pipe with oxygen, instead of air, an intensely hot flame is produced. A similar flame may be obtained by injecting oxygen into a stream of hydrogen. These flames, though not very luminous, will render quicklime incandescent, and melt such infusible substances as platinum and flint (silica, 307). The high temperatures of flames fed with oxygen instead of air may be ascribed to the fact, that all the heat generated is available for raising the temperature of the products of combustion, whilst if air be used much heat is wasted in raising the temperature of the inactive nitrogen present in the air.

129. Diffusion of gases. Place a long narrow gas cylinder filled with hydrogen, and closed with a glass plate, mouth downwards above the open mouth of a similar cylinder filled with oxygen; remove the glass plate gently, and leave the two cylinders undisturbed for a few minutes. Separate the cylinders and bring a light to the mouth of the lower cylinder. When you do this its contents will explode, which shows us that some hydrogen must have travelled, against the action of gravity, from the upper to the lower jar. If now the contents of the upper cylinder also be brought to a light, these also will explode, showing that oxygen from the lower jar has moved upwards and mingled with the lighter gas above it. When experiments are made with other gases it is found that they all mingle in a similar manner; and further, that if two vessels containing different gases are left in communication for a sufficient length of time, the contents continue to diffuse, until the two gases are equally distributed through the two vessels.

On consideration, the student will see that this remarkable property of gases must be one of the causes of the uniformity of the compo-

sition of the atmosphere. Further, he will perceive that since gases thus mix spontaneously by diffusion, they are probably composed of little masses which are in constant motion, for if gases consisted of homogeneous or jelly-like masses, or if they consisted of small particles at rest, no such spontaneous mingling would be likely to take place.

Graham's law of diffusion. By filling small bottles, provided with stoppers carrying narrow open glass tubes, with different gases such as hydrogen and carbon dioxide, placing the bottles in such positions that the ends of the open tubes were downwards for light gases, and upwards for heavy gases, leaving their contents free to diffuse into the air for fixed periods, and afterwards analysing the remaining gases, Graham discovered that hydrogen diffuses about five times as rapidly as carbon dioxide; and from the results of systematic experiments with the above and other forms of apparatus he showed *that the rates of diffusion of two gases are in the inverse ratio of the square roots of their densities*. So that in the case of oxygen and hydrogen, whose densities are as 16 to 1, their rates of diffusion are as 1 to 4*.

EXPERIMENT 102. The diffusive powers of light and heavy gases may easily be compared in the following manner. Attach a porous clay bottle *A* (Fig. 60) to a piece of glass tube *B* about 5 or 6 mm. in bore and 50 cm. in length; place the open end of *B* under some water in *C*, place a beaker over *A*, and fill it by displacement with hydrogen. Notice that gas at once escapes rapidly from *B*, owing to the fact that the light hydrogen enters *A* much more quickly than the denser air escapes. When no more gas escapes at *C*, remove the beaker. The gas inside *A* now chiefly consists of light hydrogen, and accordingly the water rapidly rises in *B*, since the hydrogen escapes from *A* more quickly than air can enter.

Applications. Since light gases diffuse more rapidly than those which are denser, we can separate the components of gaseous mixtures by diffusion; and distinguish mixtures of gases from single gases by studying their behaviour when they are allowed to diffuse.

EXAMPLE. Pass the gases obtained by electrolyzing water (Expt. 36) through the stem of a clay tobacco-pipe. You will find that the gas

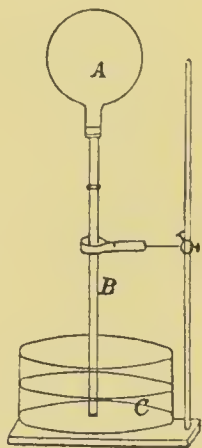


Fig. 60.

* How is the molecular weight of a gas related to its rate of diffusion?

which escapes will not detonate, as much of its hydrogen has separated by diffusion.

When studying a gas of unknown composition the chemist sometimes determines the density of the gas, then allows it to pass through a porous pipe, collects that part which diffuses, and also the fraction which escapes at the end of the porous tube, and determines the densities of the two fractions. If their densities differ from that of the original gas, he knows the former must consist of at least two constituents.

Again, the rates of diffusion of two gases may be studied in order to ascertain their densities. Soret found the density of ozone by comparing its rate of diffusion with those of chlorine and carbon dioxide (see 124).

For liquid diffusion, see 35.

130. The liquefaction of gases. It was long suspected that just as steam can be converted into water by cooling it, so the various permanent gases would become liquid if sufficiently cooled. In short, it was thought that all gases were the vapours, so to speak, of unknown liquids. This idea was strongly confirmed when Faraday (1823) liquefied ammonia (see Expt. 161), hydrogen chloride, and several other gases by generating them at one end of a sealed glass tube, like that shown in Fig. 87, and condensing them at the other end of the tube by means of freezing mixtures. Faraday was unable to liquefy hydrogen, oxygen, nitrogen, and some other gases, as he was not aware that a gas can be liquefied only when its temperature is below a particular point called its 'critical temperature' (see below). But even after this important fact was discovered, all attempts to liquefy oxygen, hydrogen and nitrogen failed until 1877, when Pictet succeeded in liquefying oxygen by cooling it to about -130° * under great pressure, and Cailletet, at about the same time, liquefied the same gas by strongly compressing it and then suddenly reducing the pressure so that its temperature might be reduced by its own rapid expansion. Subsequently Wroblewski condensed nitrogen and carbon monoxide to thin mobile liquids, and finally Dewar, whose experiments on the liquefaction of air on the large scale had long been famous, obtained liquid hydrogen in vessels open to the air on May 10, 1898.

In the earlier researches on the liquefaction of oxygen, a cooling

* This low temperature was obtained by the rapid evaporation of liquid carbon dioxide.

agent, such as boiling carbon dioxide, or ethylene, was very frequently employed, but of late the process of cooling a gas by its own expansion has been applied cumulatively, so that liquid oxygen and liquid air can now be obtained without the use of liquid carbon dioxide or ethylene and in comparatively large quantities. In the apparatus designed for this purpose, the compressed gas is allowed to pass through concentric coils of tubes, and thence to escape through a special valve. As it escapes, the gas passes from a high pressure to a lower one, and its temperature falls. After its escape the cooled gas is made to circulate outside the coils which convey the compressed gas to the valve. These coils and their contents are accordingly cooled, and thus each successive portion of gas escapes at a lower temperature than that which preceded it, until, at last, the escaping gas reaches its liquefying point. It then condenses, and is received in a vacuum vessel designed for the purpose by Professor Dewar. The portion of the gas which escapes condensation can be again compressed and transmitted through the coils to the valve. If the coils are cooled by liquid carbon dioxide before the process is started, the action of the apparatus is improved.

Critical temperatures of gases. About 1869 the late Professor Andrews observed that it was impossible to liquefy carbon dioxide by compressing it when its temperature was above 31° . This temperature is called the *critical temperature* of carbon dioxide, and it has been found that the other gases also have critical temperatures. Before Andrews' time physicists chiefly relied on the effects of pressure in their attempts to liquefy the permanent gases; but his discovery suggested better modes of working to his successors. The following table gives the critical temperature, critical pressure, and boiling-point at atmospheric pressure of two or three important gases.

	<i>Critical Temperature.</i>	<i>Critical Pressure*.</i>	<i>B. P. at Atmospheric Pressure.</i>
Hydrogen. . .	-238° to -240°	15.3 atmospheres	-252
Nitrogen . . .	-146.0	35.0 „	-194.4
Oxygen. . .	-118.8	50.8 „	-182.7

131. The kinetic theory of gases. We have learnt from

* This may be said to be the pressure which a substance exerts at its critical temperature. Substances deviate largely from the gaseous laws (63, 64), when their temperatures and pressures are near their critical values.

the preceding pages that matter may be supposed to consist of very small particles called molecules, which have characteristic qualities in the case of each different substance. That these molecules are themselves built up of still smaller particles of matter called atoms, and that chemical change consists in the rearrangement of the atoms of one set of molecules and the production of a new set in which the same atoms occur, but not grouped in the same manner as at first. But though we have formed definite ideas about the nature of chemical change, we have still to consider how the molecules are related to one another mechanically in the solid, liquid, and gaseous forms of matter; what happens when any one of these forms is transformed into another; and how far we can account for the gaseous laws by means of the same molecular hypothesis.

From what you have learnt about diffusion (129), you will at once admit that a gas must be made up of separate particles (molecules) and that these molecules must be in motion, for it is evident that two gases made up of molecules which are at rest would not mix. Further, from the relative rates of diffusion of light and heavy gases, it would appear that light molecules move more rapidly than those which are heavier when they are at the same temperature.

According to the kinetic theory of gases the molecules of a gas are constantly moving with great rapidity in straight lines, except when they come into contact with one another or with the bounding surfaces of the vessel which contains them; when this happens they rebound, moving off with undiminished rapidity in new directions*. The pressure exerted by a gas on the boundaries of the containing vessel is the result of this bombardment of the vessel by the moving molecules, and for a given mass of a given gas at a given temperature it varies inversely as the volume occupied by the gas (Boyle's Law). because the number of impacts on a given area in unit time will be inversely proportional to the volume occupied.

We have learnt from a previous section that when a given mass of a perfect gas is heated, its volume is increased by $\frac{1}{273}$ of its volume at 0° for each degree, provided that its pressure remains constant. If its *volume* be kept constant, however, its pressure increases at a corresponding rate. Under these latter conditions the number of molecules and their average distance from each other remain unchanged†;

* The molecules are supposed to behave like perfectly elastic bodies.

† Provided that no decomposition occurs.

therefore the increase of pressure must be caused by the increased speed with which the molecules move, which would enable every particle to strike the boundary of the vessel harder and also more frequently. Now the pressure of a gas at constant volume is proportional to its *absolute* temperature, and since the pressure depends on what we may call the average speed with which the molecules move the latter gives us a measure of temperature.

The Kinetic theory of gases enables us to form a distinct conception of the nature of the phenomena met with in Experiment 102, and of what occurs when the constituents of a gaseous mixture are partially separated by passing the mixture through a porous tube, surrounded by a vacuous enclosure. For if the molecules of the two gases are moving in the manner described above, but with different velocities, then the lighter molecules, which move the faster, will reach the sides of the tube more frequently than the others, and so escape by the passages provided by the porous tube more often than those which are heavier; the efficiency of the process being limited by the fact that after reaching the surrounding enclosure they will have a tendency to return to the tube by a similar process, unless they are removed.

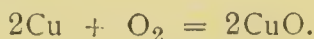
Liquids. The phenomena of liquid diffusion (35) and the slowness with which liquids evaporate make it plain that the molecules of liquids are also in motion, but that they move much more slowly than the molecules of gases. It is evident that in a liquid the molecules are under some restraint; they can slide over one another, which enables a liquid to take the form of the vessel in which we place it, but they cannot fly apart like the molecules of gases, for a liquid is not able to expand and fill an unlimited space as a gas does.

In spite of the tendency of liquid molecules to hold together, some of those near the surface of a volatile liquid are evidently able to escape and become gaseous. When this happens in a very large space many of the escaping molecules move away, i.e. evaporation occurs. But if the liquid be confined in a small closed space, as in Experiment 18, the molecules cannot go far from the liquid, and sooner or later they must return to its surface and be retained, so that presently the liquid gains and loses molecules at equal rates, provided that its temperature remains unchanged. But the rate at which a given liquid gains molecules depends on the number of molecules present in unit volume of the surrounding space and on the

speed at which they move; and these determine the vapour pressure of the liquid at any moment. Hence a volatile liquid must have a particular maximum vapour pressure (see 23) for each temperature.

In the case of solids the molecules are held together much more strongly than in liquids, and they do not readily alter their relative positions. We cannot say, however, that their particles are really at rest; indeed many solids are more or less volatile at temperatures below their melting-points. Every one must have noticed the gradual disappearance of snow during a hard frost, and we are all familiar with the odour of camphor*.

132. Oxidation and reduction, oxidizing and reducing agents. EXPERIMENT 103. An example of oxidation. Heat some copper turnings to redness in a hard-glass tube, and draw a current of air over them. The copper will soon be converted into black oxide of copper (CuO):—



This is an example of oxidation. Other simple instances of oxidation are the burning of magnesium and of coal, also of wood and other ordinary combustibles, and the oxidizing of iron filings by water-vapour (see Expt. 52).

EXPERIMENT 104. Some examples of reduction. Reheat the oxide of copper made in Experiment 103 in a current of hydrogen. It will soon become red, water-vapour will be given off, which may be condensed (Expt. 53), and metallic copper will be found in the tube at the end of the experiment:—



Repeat the last experiment, using carbon monoxide (CO)† (for its preparation, see 282). You will again reduce the oxide, copper and carbon dioxide being produced:—



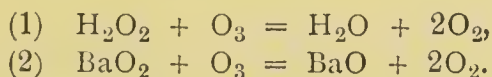
From these experiments you will see that we apply the term *Oxidation* to changes in which oxygen is added to an element or compound, and the term *Reduction* to changes in which oxygen is removed from compounds containing that element.

* Fuller discussions of this subject will be found in Dobbin and Walker's *Chemical Theory for Beginners* and in Walker's *Physical Chemistry for Beginners*.

† Coal gas, the vapour of paraffin, or any combustible vapour would give a similar result.

In a general way, substances which readily part from oxygen, like oxide of copper, are called *oxidizers*, whilst those which are apt to remove oxygen from compounds containing it, like hydrogen, iron, and carbon monoxide, are called *reducers* or *reducing agents*.

If the student will inspect the illustrative equations given above, he will observe that the oxidation of one substance is usually accompanied by the reduction of another, for one substance cannot gain oxygen unless some other substance loses it; but it sometimes happens that two powerful oxidizers act upon one another in such a manner that both are reduced. Thus if ozone (O_3) be allowed to act on hydrogen peroxide (H_2O_2) or on dioxide of barium (BaO_2) (Thorpe) the following reactions are said to occur:—



The word oxidation was formerly almost synonymous with combustion, but the terms oxidation and reduction are no longer confined to changes in which oxygen plays a part. For example, chlorine is said to oxidize iron when they combine, and also when it converts ferrous chloride ($FeCl_2$) into the ferric salt ($FeCl_3$); and ferric chloride is said to oxidize hydrogen sulphide (H_2S) when they interact as shown in the following equation:—



In short, any chemical change in which a negative radicle, either simple or compound, is added to a more positive radicle, or any chemical change which effects a decrease in the relative amount of the positive radicle of a compound may be termed an oxidation. On the other hand the term reduction may be applied to any change which involves a decrease in the relative amount of the negative radicle present in a compound.

EXPERIMENT 105. To study the action of some other oxidizing agents. Many substances will act as oxidizing agents, but only a few of them are much used in practice. The following are among the most important of these, and the experiments described will illustrate their mode of action. *Ozone*: see 124.

Chlorine. Dissolve a few iron filings in some dilute hydrochloric acid, and add excess of alkali to a drop of the filtered solution. Notice that a bluish-green precipitate is thrown down; this consists mainly of ferrous hydroxide (FeH_2O_2). Then pass chlorine through

the rest of the solution, and warm it until the liquid acquires the odour of chlorine. If you add alkali to the product, a brown precipitate of ferric hydroxide ($\text{Fe}_2\text{H}_6\text{O}_6$), will fall.

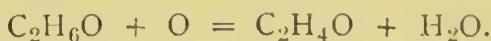
Nitric acid, and nitre. Boil some solution of ferrous chloride with a little strong nitric acid. On adding alkali you will again find that ferric hydroxide is precipitated.

Fuse some chromic oxide (Cr_2O_3) with nitre in a dish. Notice that the green oxide of chromium dissolves forming a yellow fluid. The colour is due to the presence of potassium chromate (K_2CrO_4).

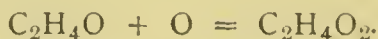
Make similar experiments with carbon and copper, examining the gas given off in each case for carbon dioxide, oxygen and nitrogen, and try to ascertain whether the former produces any carbonate, and what happens to the copper.

Potassium chlorate. Cautiously drop small fragments of sulphur into some fused chlorate of potassium. Notice the effect produced. Allow the residue to cool, and dissolve it in water; add a drop or two of solution of barium chloride (BaCl_2) and a few drops of a dilute solution of hydrochloric acid to the solution. A copious white precipitate of barium sulphate (BaSO_4) will fall.

Chromic anhydride (CrO_3) *or chromic acid* (H_2CrO_4). Dissolve a little potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in water, add some strong sulphuric acid, to liberate chromic acid (H_2CrO_4), then a drop or two of rectified spirit (alcohol $\text{C}_2\text{H}_6\text{O}$) and warm the mixture. It will soon acquire the characteristic odour of *aldehyde* ($\text{C}_2\text{H}_4\text{O}$). This is formed by the removal of hydrogen from the alcohol:—



If the action of the oxidizer be carried further, acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) (299) will be formed:—



In these changes oxygen is supplied to the alcohol at the expense of the chromic acid, the latter being reduced and converted into a salt of chromium. Accordingly the colour of the solution alters from yellowish red to green * during the experiment.

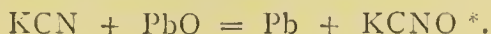
Potassium permanganate. Illustrations of the use of this substance as an oxidizing agent will be found in Experiments 299 and 300.

EXPERIMENT 106. To study the action of some reducing agents. The following are among the most important reducing agents.

* Many of the salts of chromium are green.

Carbon in the form of charcoal and small coal is largely used for obtaining the metals from their ores.

Potassium Cyanide (KCN). Melt a little potassium cyanide in a crucible or iron spoon, and add, little by little, some oxide of lead (PbO). The oxide will quickly be reduced by the cyanide, and a globule of molten lead will form at the bottom of the dish :—



Several other oxides may be reduced in a similar manner.

Hydrogen sulphide (H₂S). Add a little sulphuric acid to some solution of potassium bichromate (K₂Cr₂O₇), then pass a stream of hydrogen sulphide (183) through the solution. The red colour of the bichromate will quickly change to green, owing to the formation of a salt called chrome alum (K₂SO₄.Cr₂(SO₄)₃.24H₂O), and a precipitate of sulphur will form.

Sulphur dioxide (SO₂). Repeat the last experiment, using sulphur dioxide instead of hydrogen sulphide, and observe whether a similar change is effected.

Hydrogen and carbon monoxide are also powerful and valuable reducing agents. For an important application of the latter see the Blast Furnace (489).

The compounds of hydrogen with oxygen, viz. water and hydrogen peroxide, have already been studied. Its compounds with the other elements include the acids and many very important substances, such as ammonia (217) and the hydrocarbons (291–294). These will be studied at later stages.

CHAPTER XIII

INTRODUCTION TO THE 'PERIODIC LAW'

133. The connexion between the properties of the elements and their atomic weights—Prout's hypothesis.

From the early days of the atomic theory chemists have sought to discover the existence of some relation between the properties of the elements and their atomic weights, and more than eighty years ago it was suggested that the atomic weights of the elements (taking the atomic weight of hydrogen as unity) were multiples of the atomic weight of the lightest element. The truth of this suggestion has

* KCNO potassium cyanate.

never been demonstrated *, but Prout founded upon it the hypothesis 'that hydrogen may be regarded as the primary matter from which the other elements have been formed by condensations.' This hypothesis was never placed on a secure basis by Prout or his successors, but it has played an important part in Chemistry, by promoting investigations bearing on the atomic weights of the elements.

134. The periodic law. We have learnt that the elements may, broadly speaking, be divided into two large groups, the metals and the non-metals; those which are electro-positive to hydrogen, and those which are electro-negative, or again, those which tend on the whole to produce basic oxides, and those whose oxides are more apt to be acidic. But chemists have long recognized the existence of other lines of division, and have made various attempts to systematize the study of chemistry by arranging the elements in small groups, or families, of more or less closely related substances. All these attempts have of late been merged in a system of classification based upon 'the periodic law' † (see below). The student will not fully understand the periodic system of classification at present, but, as a general idea of its scope will be helpful to him, it may be studied with advantage, though of necessity in a very imperfect form, at this early stage.

When the known elements are arranged in the order of their atomic weights, certain blank spaces being left for others which may possibly exist but which are still undiscovered, it is found that those elements which most closely resemble one another, occur at more or less regular intervals or periods in such a manner that a table can be constructed, like that which follows, on p. 181, in which groups of more or less similar elements fall vertically above one another, whilst series of dissimilar elements make up the horizontal lines of the table.

The real significance of this system of classification will appear gradually as you study the various groups of elements in detail; but it may be pointed out in advance, by way of illustration, that the elements lithium, sodium, potassium, rubidium and caesium, which are characteristic members of Group I in the table, are all univalent metals, which decompose cold water, and form soluble and very alkaline hydroxides; and similarly that, omitting manganese, Group VII consists of four univalent non-metals which form acids, like hydrochloric acid,

* A very considerable number of the best determined atomic weights fall within one-tenth of a unit of whole numbers.

† Which we owe to the late Mr. Newlands and others, among whom Professor Mendeleeff and the late Professor Lothar Meyer have been most conspicuous.

TABLE TO ILLUSTRATE THE PERIODIC SYSTEM OF CLASSIFYING THE ELEMENTS.

(Approximate atomic weights only are given in this Table. See also p. 47.)

Series	O*	I	II	III	IV	V	VI	VII	VIII
		K ₂ O	RO	R ₂ O ₃	RO ₂ RH ₄	R ₂ O ₅ or R ₄ O ₁₀ RH ₃	RO ₃ RH ₂	RH	
1		H 1							
2	He 4	Li 7	Be 9	B 11	C 12	N 14	O 15.9	F 19	
3	Ne 20	Na 23	Mg 24	Al 27	Si 28.2	P 31	S 32	Cl 35.2	
4	Ar (39.6?)	K 39	Ca 40	Sc 44	Ti 48	V 51	(Cr 52)	(Mn 54.5)	{ Mn 54.5 Fe 55.6 } { Co 58.5 Ni 58.2 } { Cu 63 }
5		(Cu 63)	Zn 65	Ga 69.4	Ge 72	As 74.4	Se 78.4	Br 79.3	
6	Kr 81	Rb 85	Sr 87	Y 88.4	Zr 89.7	Nb 93	Mo 95.3		{ Ru 101 Rh 102 } Pd 105.5 (Ag 107)
7		(Ag 107)	Cd 111	In 113	Sn 118.2	Sb 119.5	Tel 126.5?	I 126	
8	Ne 127	Cs 132	Ba 136.4	La 137.6	Ce 139				
9		?	?	?	?	?	?	?	
10			?	?		Ta 181.5	W 183		Ir 191.5 Pt 193.4 (Au 195.7) Os 189.5
11		(Au 195.7)	Hg 198.5	Tl 202.6	Pb 205.4	Bi 206.5			
12		?	Ra (?)		Th 231		U 237.8		

* Since this Table was drawn up an entirely new group of elements has been discovered. These are Helium, Neon, Argon, Krypton, Xenon. They are distinguished for their want of any distinct tendency to combine, and, as will be seen in the present Table, form the new Zero group now introduced for the convenience of teachers. See also p. 259.

with hydrogen, which are all remarkable for the readiness with which they combine with metals, for their volatility, and for the colours and odours of their vapours. On the other hand, if the first seven elements are studied, they are found to differ from each other in a somewhat regular manner. Thus lithium is univalent, and is a metal which decomposes cold water; beryllium is divalent, and is also a metal; boron is trivalent, and is a non-metal, forming an acid oxide; carbon is quadrivalent, and is also a non-metal, and so on till we reach fluorine, which forms an acid with hydrogen.

The two groups and the series thus briefly described illustrate the periodic system of classification almost too well, and it must not be supposed that the members of all the groups exhibit so close a resemblance, nor that the members of every series exhibit such a regular gradation in their qualities, as those of the group and series selected for the purpose of illustrating the law. The discussion of details must be postponed for the present, but it may be added that since the law was enunciated, several new elements have been discovered (Sc, Ga, Ge), which readily fall into the positions that were assigned to them, in advance, when the table was drawn up *. And that in one case especially, viz. that of tellurium, the new system of classification has been useful by affording us a means of checking its atomic weight.

The following concise statement of the 'periodic law' has been proposed by Prof. Hartley—'The properties of atoms are a periodic function of their masses.'

The above statement concerning the periodic law might lead the student to suppose that it only applies to the chemical properties of the elements, but this is not so. The law also applies to some of their physical properties, though not to all †. In order that this may not be lost sight of the following brief account of specific volumes and atomic volumes should be read carefully.

SPECIFIC VOLUME, ATOMIC VOLUME, AND THE PERIODIC LAW.

Specific volume. We have learnt that the relative masses of equal volumes of solids, liquids and gases are known as their *densities*. On the other hand, the volume occupied by unit mass of a substance, which is inversely proportional to its density, is known as its *specific volume*.

* The position of the new constituents of atmospheric air is still under discussion.

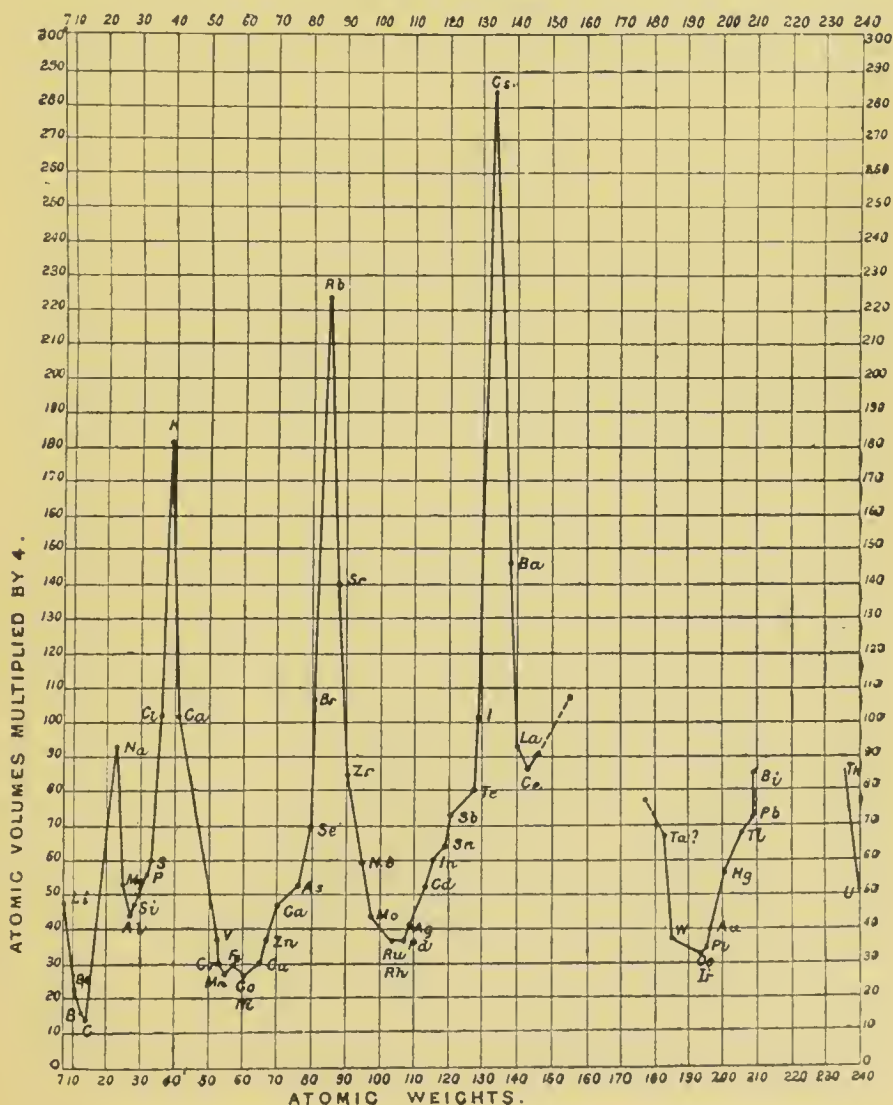
† See specific heat (95).

Thus the weight of 1 c.c. of water is one gram, that of 1 c.c. of lithium is 0.59 gram. Therefore their relative specific volumes are :—

$$\text{Water } \frac{1}{1} = 1. \quad \text{Lithium } \frac{1}{.59} = 1.7.$$

Atomic volume. If the volume occupied by unit mass of an element be multiplied by its atomic weight we obtain its *atomic volume*. Thus the atomic volume of lithium is :—

$$1.7 \times 7 = 11.9.$$



The atomic volumes of the elements are plotted as a curve on the previous page. The student should inspect this curve, and compare the positions occupied by the elements which make up each group and series under the periodic classification; he should also notice whether the non-metals all appear on the upward or downward slopes * of the curve. Several other physical properties, e.g. fusibility, also exhibit a periodic character, but in most cases want of data makes it impracticable to be sure of the truth of the relations suggested. The atomic heats of the elements, on the other hand, exhibit no such relations (see 95), but approximate to the constant 6.4.

CHAPTER XIV

THE HALOGENS

CHLORINE, bromine, iodine, and fluorine, form one of the groups shown in the table on p. 181. Owing to the marked resemblance between these elements and their compounds, it will be convenient to study one of them, chlorine, rather minutely, and the rest in less detail.

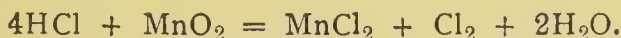
CHLORINE (Cl_2): Atomic weight, 35.18.

135. The discovery and preparation of chlorine. When common salt is heated with oil of vitriol a colourless acid gas is evolved, and for many centuries a solution of this gas in water was known as 'spirit of salt,' and later as muriatic acid. The gas itself was first carefully examined by Priestley in 1774. In the same year Scheele obtained a green gas, possessed of an intolerable odour, by treating the solution of muriatic acid with the mineral pyrolusite, which contains manganese dioxide (MnO_2). This latter gas was named oxymuriatic acid by Berthollet, on the assumption that it was a combination of muriatic acid and oxygen, but in 1810 Sir Humphry Davy (see 110) showed that there were no sufficient grounds for this assumption, and since then the green gas has been regarded as an element, and known by the name of chlorine.

* The curve is supposed to start from lithium.

Chlorine occurs in nature only in combination. Large quantities are found in the form of common salt (NaCl); potassium chloride (KCl) and magnesium chloride (MgCl₂) are also plentiful, and other chlorides are met with in smaller quantities. Hydrogen chloride is among the gases given off by volcanoes.

EXPERIMENT 107. To prepare chlorine. Place 1 part of granular manganese dioxide (MnO₂*) in a flask provided with a thistle funnel and a delivery tube (*A*, Fig. 63), moisten the oxide slightly with water, then pour upon it about 10 parts of strong solution of hydrochloric acid, and warm the contents of the flask. A gentle effervescence will be set up, and a yellowish-green suffocating gas will be evolved, whilst manganous chloride (MnCl₂) and water will remain in the flask:—



The experiment should be made in the open air, or in a fume chamber provided with a flue for carrying off excess of chlorine.

The chlorine may be dried, if necessary, by passing it over fragments of calcium chloride in a U tube. It may be collected, in glass cylinders, by *downward* displacement of air, owing to its high density, or over paraffin oil.

In order to avoid the loss of chlorine, in the form of manganous chloride, which occurs in the above process, a mixture of salt and black oxide of manganese may be warmed with sulphuric acid. All the chlorine is said to be liberated, if proper proportions of the chemicals are employed:—



but no real economy is effected owing to the cost of the sulphuric acid.

N.B.—Chlorine is injurious if inhaled. The following experiments should therefore be performed by the teacher.

136. Some properties of chlorine. **EXPERIMENT 108.** To observe the direct formation of metallic chlorides. 1. Introduce a sheet of Dutch metal and a little powdered antimony into two jars

* Other peroxides or potassium bichromate may also be used.

containing chlorine. The metals will inflame spontaneously, absorbing the chlorine and forming chlorides.

2. Melt a piece of sodium in a hard-glass tube (Fig. 64), and pass chlorine through the tube. The sodium will burn with a brilliant golden glow, forming a white solid which, if cautiously tasted, will be found to have the flavour of common salt (NaCl).

3. Heat a globule of quicksilver cautiously in a stream of chlorine. A flame will play over the surface of the metal, and a white crystalline sublimate of mercuric chloride (HgCl_2) will condense on the cooler parts of the tube.

The readiness with which chlorine unites with most metals is one of its most characteristic qualities.

EXPERIMENT 109. The action of chlorine with non-metals.

1. Plunge a fragment of phosphorus in a deflagrating spoon into a jar of chlorine. It will at once inflame, producing pentachloride of phosphorus (PCl_5), unless there be excess of phosphorus, in which case the trichloride (PCl_3) may be formed.

2. Place some flowers of sulphur in a jar of chlorine. You will see no signs of combination in this case, though sulphur and chlorine combine at higher temperatures.

3. Place some charcoal in chlorine. You will find that it is unaffected by the gas.

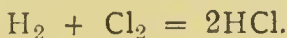
4. Soak a piece of blotting-paper with turpentine ($\text{C}_{10}\text{H}_{16}$), warm it gently, if the room be cool, and plunge it into a jar of chlorine. The turpentine will quickly burst into flame, giving off clouds of carbon mixed with irritating fumes of hydrogen chloride (HCl).

If you plunge a lighted taper into a jar of chlorine you will obtain a similar result. It is not, however, impossible to obtain compounds of chlorine with carbon. Thus, when a mixture of marsh gas (CH_4) (291) and chlorine is exposed to diffuse sunlight the following compounds may be formed by replacement of the hydrogen of the marsh gas: methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform (CHCl_3), and carbon tetrachloride (CCl_4).

Chlorine also combines with various unsaturated carbon compounds, such as carbon monoxide (CO), forming COCl_2 ; ethylene (C_2H_4), forming $\text{C}_2\text{H}_4\text{Cl}_2$; and with sulphur dioxide (SO_2).

5. *Chlorine and hydrogen.* Place a jar of hydrogen covered with a ground glass plate mouth upwards on the table, and stand upon it, mouth downwards, a jar of chlorine, slip aside the glass plates, leaving the open jars mouth to mouth; when the gases have mixed bring

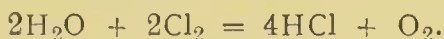
a light to the mouth of one of the jars. The mixture will explode with great violence. Notice that clouds of a fuming acid gas are produced, and that the contents of the jar are no longer green after the explosion. The gases have united forming hydrogen chloride, the well-known 'muriatic acid gas' (141):—



Chlorine a disinfectant. Chlorine is sometimes used as a disinfectant. It destroys the minute organisms which play an important part in the processes of putrefaction and decay, and which are believed to cause many diseases.

EXPERIMENT 110. To study the action of chlorine with water.

1. Pass chlorine and steam simultaneously through a glass tube heated to redness, and collect the gas which escapes over water. You will find it to be oxygen. The solution formed will be acid to litmus, for it contains hydrogen chloride:—



2. Half fill a bottle with saturated solution of chlorine in water, fill up the bottle with chlorine, close it securely, and expose it to sunlight. When the colour of the chlorine has disappeared, open the bottle and examine its contents. You will find that the gas which remains consists chiefly of oxygen, and that the liquid has become acid, for chlorine has again liberated oxygen from water and combined with its hydrogen*.

Owing to the power possessed by chlorine of liberating oxygen from water, chlorine water acts as an oxidizing agent.

3. Pass chlorine through some dilute solution of sodium hydroxide in which finely powdered sulphur is suspended. Filter the liquid, and test it for a sulphate. You will find that the sulphur has been oxidized.

EXPERIMENT 111. The bleaching action of chlorine. 1. Pass a few bubbles of chlorine into some solution of indigo. The chlorine will rapidly convert the latter into a nearly colourless compound.

2. Make a broad mark upon a printed label with writing ink; when the ink is dry, plunge the label into a jar of chlorine. The writing ink, which owes its blackness to the presence of organic colouring-matter, will be quickly bleached, but the printed matter will remain

* These are not usually the sole products of the change however; hypochlorous acid is also formed.

unaffected, because its blackness is due to finely divided carbon, which is not attacked by chlorine.

3. Place some chlorine in a gas jar, together with some lumps of calcium chloride; close the cylinder with a well-greased glass plate, and expose the chlorine to the chloride of calcium. Dry some Turkey red twill in an air bath, and place it in the dried chlorine.

At the same time place a piece of moist red twill in a jar of undried chlorine.

You will find that the dried chlorine bleaches the twill far less rapidly than that which is moist. This result suggests the idea that the bleaching may have been caused by the combined action of chlorine and water; viz. that the chlorine may have liberated oxygen from the water, and that this may have attacked the colouring matter.

137. Nascent state. But Turkey red twill, and other coloured fabrics are, as we well know, constantly exposed to the oxygen of the air without much loss of colour. How then can oxygen be the bleaching agent in the above experiments?

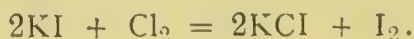
To explain this, it has been pointed out that if a molecule of water were decomposed by a molecule of chlorine, a single atom of oxygen might very possibly be liberated momentarily:—



and that such a single atom would probably be more active as a bleaching agent, and in other ways, than the same atom would be after it had again entered into combination to form a molecule of oxygen. The term *nascent oxygen* has been applied to the element in this hypothetical condition. Analogous phenomena may be observed in the case of other elements.

For example, aqua regia, a mixture of nitric and hydrochloric acids which gradually generates chlorine (138, 2), attacks gold and platinum more vigorously than free chlorine.

EXPERIMENT 112. The action of chlorine on compounds containing bromine and iodine. 1. Pass a bubble of chlorine into some solution of iodide of potassium. The solution will turn brown, and if some freshly made starch water be afterwards added to it will exhibit the blue colour of iodide of starch (see 165, 6), owing to the chlorine having liberated some iodine:—



If some of the solution containing free iodine be shaken with a drop or two of chloroform, a fine purple-coloured solution of iodine, in chloroform, will sink to the bottom of the liquid.

2. Add chlorine slowly to a little solution of potassium iodide, continuing to add it after the liberation of iodine has commenced. Notice that a precipitate of iodine forms, and then gradually disappears again (see iodic acid, 169).

Make similar experiments using potassium bromide.

EXPERIMENT 113. To detect chlorine in the chlorides. We have seen that the properties of an element are usually much modified after it has combined with another element. Therefore, we must not expect the compounds of chlorine to possess the odour or colour of that gas, nor to unite with metals. On the other hand, the compounds of a given element usually possess certain common qualities, which we can use as *tests*, and which, in a certain sense, may be regarded as properties of the element, since they are only exhibited by its compounds. Thus, compounds containing chlorine answer to the tests which follow :—

1. Warm a small portion of any chloride with black oxide of manganese, and some sulphuric acid. It will give off chlorine, which may be recognized by its colour, smell, and action on potassium iodide.

2. Add a drop of solution of nitrate of silver to a solution of any chloride. Notice that a colourless precipitate falls, which darkens when exposed to light, and which does not dissolve in nitric acid. This is silver chloride (AgCl) :—



Repeat the experiment, using other soluble chlorides, and notice whether similar results are obtained.

3. Add a little solution of lead nitrate to a solution of a chloride. A precipitate of lead chloride (PbCl_2) will fall. Heat this precipitate, or some of it, in some water. It will redissolve, but will reappear in crystals if the solution be afterwards cooled.

138. Other reactions by which chlorine may be generated. 1. Warm some hydrochloric acid with a crystal or two of potassium chlorate (KClO_3). The gas set free in this case resembles chlorine, but is a mixture which contains one of the oxides

of chlorine. It was at one time called *euchlorine*, under the belief that it was a peculiar form of chlorine.

2. Warm some hydrochloric acid with a few drops of nitric acid. The gas evolved contains chlorine, together with *nitrosyl* chloride (NOCl):—



This mixture is known as *aqua regia*, and is much used as a solvent. Its activity is probably mainly due to *nascent* chlorine.

3. Warm some hydrochloric acid with some chromic anhydride (CrO_3), or potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$):—



4. *Deacon's process*. In this process a mixture of air and hydrochloric acid is passed over pumice-stone encrusted with a salt of copper, and heated to about 400° . As the copper salt acts continuously, successive supplies of hydrochloric acid can be oxidized in this way. This process is sometimes used on the manufacturing scale. The change may be represented as follows:—



5. *Chlorine and soda are manufactured by the electrolysis of salt.*

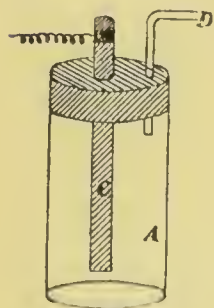
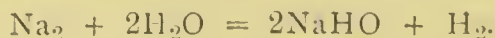


Fig. 61.

EXPERIMENT 114. Place strong brine in a small 'porous pot' *A*, provided with a cork carrying a rod of carbon *C*, and a delivery tube *D* (Fig. 61). Stand *A* in a jam-pot, also filled with brine. Connect *C* with a galvanic battery, and connect the same battery with a sheet of platinum immersed in the brine in the outer pot, making *C* the anode. When this is done, bubbles of hydrogen will rise from the platinum plate, and the odour of chlorine may soon be detected at *D**. If the contents of the outer vessel are examined, they will be found to be strongly alkaline, owing to the

presence of sodium hydroxide formed from the sodium by the action of water:—



The porous pot *A* is employed to prevent the chlorine and the soda (NaHO) from mingling, except very slowly, because soda and chlorine produce bleaching solution (see 150).

* Why is a carbon electrode used in *A*?

139. Recovery of manganese dioxide—Weldon's process.

Enormous quantities of manganese dioxide are used by manufacturers of chlorine, and it is important to them to reoxidize the manganese which remains in liquor from which the chlorine has been expelled. In Weldon's process, which is very largely used for this purpose, the solution of manganese chloride is shaken with calcium carbonate to neutralize free acid and precipitate iron as oxide; then warmed with a certain excess of slaked lime (CaH_2O_2) to about 55° , and exposed to the action of air, which is forced into it by blowing machines. As the result of these operations a precipitate is formed, which contains manganese and calcium, and is rich in oxygen. This is separated and used to oxidize further portions of hydrochloric acid.

The tendency of oxide of manganese to absorb oxygen may easily be seen by adding alkali to a solution of a salt of manganese in a flask, and agitating the contents of the flask with air. When this is done the light-coloured manganese hydroxide (MnH_2O_2), first thrown down, rapidly turns brown owing to the forming of higher oxides.

140. Further account of the properties of chlorine.

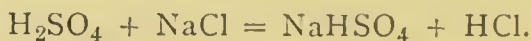
Chlorine has a greenish-yellow colour which darkens under strong pressure. It does not obey the laws of Charles and Boyle below 240° . It is readily condensed to a pale yellow liquid by a freezing mixture composed of solid carbon dioxide and ether. In the liquid form it is considerably heavier than water ($D = 1.47$ at 0°), and boils at -33.6° . Its critical temperature is about 140° ; its critical pressure about 94 atmospheres. When well dried it is without action on iron, and the liquefied gas can be preserved for long periods in iron or steel bottles. It has been solidified. As in the case of oxygen, its chemical activity is, in some cases, dependent on the presence of moisture, for well dried chlorine acts very slowly on copper, sodium, and some other metals. It acts rapidly on mercury, however, even after the most careful and prolonged drying. Chlorine is more soluble in water than oxygen; if it be passed into water at 0° , crystals of a hydrate ($\text{Cl}_2 \cdot x\text{H}_2\text{O}$) are formed. If some of these are drained, and warmed in a sealed tube, they yield the liquefied element.

Chlorine has very little attraction for oxygen, and its oxides are all very instable (see 154).

141. Hydrochloric acid (HCl), density, 18.1. Synonyms: muriatic acid, spirit of salt. We have seen that free hydrogen

and chlorine readily combine, but hydrochloric acid is usually prepared as a by-product in the 'salt-cake process' (see 357, 1).

EXPERIMENT 115. To prepare hydrochloric acid as gas and in solution. Heat 1 part of salt in a flask *A* (Fig. 63), provided with a delivery tube *E*, with 2 parts of sulphuric acid. A colourless, fuming gas will be evolved, and sodium hydrogen sulphate (NaHSO_4) will remain in the flask :—



This gas may be collected by displacement of air or over quicksilver, but not over water.

Fill a large flask *A* (Fig. 62) with hydrochloric acid gas by means of a delivery tube *C*. Remove *C*, and plunge the open end of *D* in a basin of water tinged with blue litmus. The water will rush into *A* almost as rapidly as if the flask had been exhausted.

Owing to its great solubility hydrochloric acid is usually preserved in the form of an aqueous solution. Such a solution, made at the ordinary temperature (15°), may contain about 450 volumes of the gas

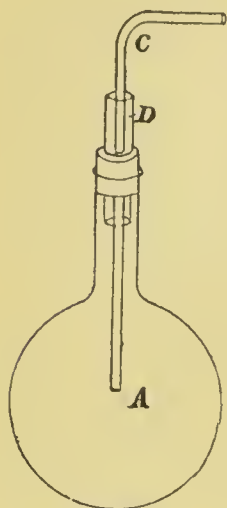


Fig. 62.

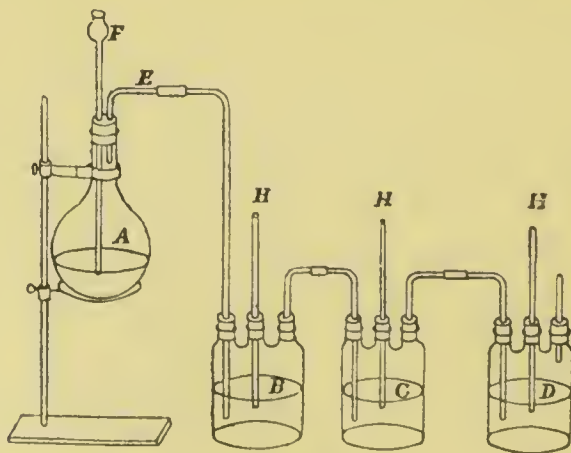
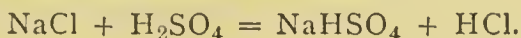


Fig. 63.

in each volume of water, or 40.7% by weight, and will have a density of 1.20 (water = 1).

The process of making solution of hydrochloric acid should be carefully studied as solutions of other gases are made in a similar manner.

Heat salt and sulphuric acid in proper proportions in *A* (Fig. 63), and wash the gas with water in *B*, *C*, and *D*, until it begins to escape from *D*. The solution made in *C* will be of the best quality, but that formed in *B* contains minute portions of salt, sodium sulphate, and sulphuric acid which have been ejected from *A*. The water in *D* prevents the escape of acid fumes into the air towards the end of the process, and does not become saturated unless the process is unduly prolonged. The following reaction occurs:—



The tubes *F* and *H H H* serve as safety-valves; they admit air to *A*, *B*, *C*, and *D*, in case a partial vacuum should be produced in any part of the apparatus by cooling or otherwise during the process. If at the end of your experiment you close *F*, then, as the contents of *A* cool, the solution will be drawn from *B* into *A*. On the other hand, if you leave *F* open you will see air enter through *F*.

In the 'salt-cake process,' which is carried out at a higher temperature, a smaller proportion of sulphuric acid is employed, and consequently sodium sulphate (Na_2SO_4) is formed instead of the acid sulphate:—



142. Some properties of hydrochloric acid. As its name implies, hydrochloric acid is acid to litmus. The critical temperature of hydrochloric acid is about 53° . It forms a colourless liquid at 10° under a pressure of 40 atmospheres, and solidifies below -116 ; the liquid is comparatively inactive. Its solution dissolves basic oxides and neutralizes alkalis, producing salts, or *halides*, called *chlorides*. It evolves chlorine when treated with oxidizing agents such as peroxides or nitric acid, and when electrolyzed it is split into free chlorine and hydrogen. Like other soluble chlorides it precipitates silver nitrate (Expt. 113, 2). It fumes strongly in the air, owing to its attraction for moisture, and gives very dense fumes with ammonia, which consist of ammonium chloride (NH_4Cl).

143. Properties of solution of hydrochloric acid. Solution of hydrochloric acid is used as a solvent in many chemical processes, e.g. for extracting the calcium phosphate from bones; and in tin-plate works for cleaning sheet iron; and also as a source of chlorine. A pure solution of hydrochloric acid is nearly colourless, and leaves no residue when evaporated in a platinum basin. If

diluted, it will give no precipitate of barium sulphate when a drop of solution of barium chloride is added to it. The strongest acid ($D = 1.20$) contains about 41% of real HCl. When such a solution is heated, it gives off hydrogen chloride, until a residue boiling at 110° and containing 20.22% of real acid remains. On the other hand, if a weaker acid be boiled it loses water and becomes stronger. It was once supposed that the solution containing 20.22% of acid might consist of a definite hydrate, but Sir Henry Roscoe and the late Prof. Dittmar have shown that the composition and boiling-point of the residue depend upon the pressure under which the acid is distilled. If hydrochloric acid gas be passed into some of the strongest solution cooled to -22° , it deposits crystals of a hydrate.

The hydrochloric acid of commerce is usually of a pale yellow colour, and contains ferric chloride, traces of arsenic and sulphuric acid. If it be diluted and distilled it can be freed, to a great extent, from these impurities.

144. To find the composition of hydrochloric acid.

We have already become acquainted with the grounds on which Davy concluded that this acid contains no oxygen (110), and have seen that hydrogen and chlorine yield a colourless fuming gas, said to be hydrogen chloride, when they combine (Expt. 109, 5). The following further experiments may, however, be made:—

EXPERIMENT 116. 1. To detect hydrogen in hydrochloric acid gas. Pass a current of hydrochloric acid over fragments of sodium

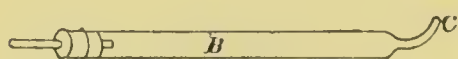


Fig. 64.

heated in a hard-glass tube *B* (Fig. 64) and apply a light at *C*. The colourless gas which escapes will burn, and water may be condensed from its flame on a cold surface. As sodium is an ele-

ment, the hydrogen which must be present in this water can only have come from the hydrochloric acid.

2. To detect chlorine in hydrochloric acid. Repeat the above experiment, using fragments of manganese dioxide in place of sodium. A gas which exhibits the qualities of chlorine will escape at *C*. If it be admitted that manganese dioxide contains no chlorine, this must have come from the hydrogen chloride.

3. These results show that hydrogen chloride contains hydrogen and chlorine, but they do not prove that no other element is present. This can, however, be established by the following experiment:—

Obtain a glass tube about 1 metre in length, and 1.5 cm. in diameter, provided with a stopper at each end, and divided into two chambers by a stop-cock. The volumes of the two chambers may conveniently be in the ratio of 1 to 2. Fill the smaller chamber with chlorine, and the larger one with hydrogen by displacement. Open the stop-cock so that the gases may mix, and expose them to sunlight. When all the chlorine has disappeared, open one end of the tube under mercury and notice that little or no contraction occurs. Then introduce a little water above the mercury and notice that two-thirds of the gas quickly dissolves. Afterwards examine the aqueous solution and the residual gas. You will find that the former is acid, and acts like hydrogen chloride with silver nitrate, also that the residual gas is hydrogen. Thus we see that only hydrogen and chlorine are required to produce hydrogen chloride, and that these gases combine in equal volumes without contracting.

4. To find the proportions of hydrogen and chlorine in hydrogen chloride electrolytically. Fill an electrolytic cell (Fig. 65), similar to that employed for decomposing water but provided with electrodes *EE* made from rods of gas carbon, with a strong solution of hydrogen chloride to the level *aa*.

Open the taps *tt*, and connect the electrodes with your galvanic battery. At first hydrogen will escape freely from the negative electrode, but no gas will rise from the positive electrode owing to the solubility of chlorine in water. After about twenty minutes, when the gas rises rapidly from both electrodes, close *t* and *t*. You will now find that chlorine and hydrogen are evolved in nearly equal volumes, but that the hydrogen is still slightly in excess.

From the above result, and from Gay-Lussac's law of volumes (83), we may conclude that hydrogen and chlorine are present in hydrogen chloride in equal volumes. Now the densities (i.e. the weights of equal volumes) of the two gases are 1 and 35.2. Therefore 1 part of hydrogen must combine with 35.2 parts of chlorine to form 36.2 parts of hydrogen chloride.

EXPERIMENT 117. Analysis of hydrochloric acid gas by the action of sodium. The composition of hydrochloric acid may be more accurately found by studying the action of sodium on the gas.



Fig. 65.

Fill a glass tube *A* (Fig. 66), about 40 cm. long and 1 cm. in diameter, with dry quicksilver, taking care to remove all bubbles, invert it in a basin of mercury *B*, and pass some hydrochloric acid gas into *A*. Let the volume of this gas V^1 be 27.7 c.c. at 22° , let the barometric pressure be 778 mm., and let 68 mm. be the height of the mercury h^1 in *A*.

Then the volume of gas taken at 0° and 760 mm. will be (see 63, 64) :—

$$27.7 \times \frac{273}{273 + 22} \times \frac{778 - 68}{760} = 24 \text{ c.c.}$$

Introduce some clean fragments of sodium into *A* *. The gas will gradually contract. When this contraction is complete, note the volume of the residue V^2 and also its temperature, the pressure of the air, and the height h^2 of the column of mercury in *A*. Let these be 13.6 c.c., 12° , 780 mm., and 80 mm. respectively. Then the volume of the hydrogen under standard conditions will be :—

$$13.6 \times \frac{273}{273 + 12} \times \frac{780 - 80}{760} = 12 \text{ c.c.}$$

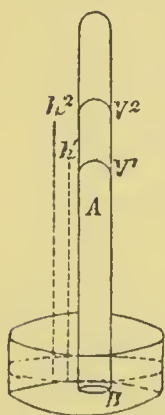


Fig. 66.

That is to say, 24 c.c. of hydrogen chloride contain 12 c.c. of hydrogen, or 2 volumes of hydrogen chloride contain 1 of hydrogen.

Now the density of hydrogen chloride is 18.1, and that of hydrogen 1.

Therefore the weights corresponding to the above volumes are :—

Hydrogen (1×1) = 1 part.

Hydrogen chloride (18.1×2) = 36.2 parts.

It follows that 36.2 parts of hydrogen chloride contain $36.2 - 1 = 35.2$ parts of chlorine and 1 part of hydrogen.

Caution. The student may perhaps wonder why we do not calculate the volume of the chlorine more simply by subtracting the volume of the hydrogen found from that of the hydrogen chloride taken. But this may not be done, because gases frequently contract when they combine (Expt. 55), so that 12 c.c. of hydrogen might conceivably combine with 12 c.c., or with 24 c.c., or with 36 c.c. of chlorine, and yet only produce 24 c.c. of hydrogen chloride.

* This must be quite free from hydroxide.

Finally calculate the percentage composition of hydrochloric acid.

Since 36.2 parts of hydrogen chloride contain 1 part of hydrogen

$$100 \quad , \quad , \quad , \quad , \quad \frac{1 \times 100}{36.2} = 2.76.$$

Therefore the percentages of hydrogen and chlorine in hydrochloric acid are :—

$$\begin{array}{rcl} \text{Hydrogen} & . & . & . & . & . & = & 2.76 \\ \text{Chlorine} & . & . & . & . & . & = & 97.24 \\ & & & & & & & 100.00 \end{array}$$

145. Why we give hydrogen the formula H_2 . It is now possible to explain why 2 was selected for the weight of a molecule of hydrogen in 91.

We have just learnt that any volume v of hydrogen will combine with an equal volume v of chlorine to form $2v$ of hydrogen chloride.

It follows from Avogadro's hypothesis (91) that m molecules of hydrogen enter into the production of $2m$ molecules of hydrogen chloride.

Or, eliminating m , that 1 molecule of hydrogen can contribute to the formation of 2 molecules of hydrogen chloride.

But each molecule of hydrogen chloride must contain at least one atom of hydrogen, for atoms are indivisible.

Therefore each molecule of hydrogen must contain at least 2 atoms of hydrogen.

It can be shown, from similar considerations, that chlorine and oxygen have also diatomic molecules. The student should endeavour to set out the argument in these two cases.

146. The chlorides. These brief statements should as far as possible be verified by experiments. Compounds of chlorine which contain no oxygen are called *chlorides*. We have already met with several instances of the forming of such compounds by direct combination (see Expt. 108). Metallic chlorides may also be made by dissolving the metals*, or their oxides, or carbonates, in hydrochloric acid, and evaporating the solutions thus obtained. Several, however, react with water. Thus a solution of bismuth chloride in small excess of acid is partly precipitated as oxychloride of bismuth ($BiOCl$) on dilution (see 471); antimony chloride behaves in a similar manner

* Those of lead, silver, and mercurous chloride are exceptions. [Why?]

(464) ; and ferric chloride, chromic chloride, and aluminium chloride are destroyed if we attempt to concentrate their aqueous solutions by boiling. These compounds have accordingly been prepared by a dry method, in which the oxide of the metal is exposed to the simultaneous action of carbon and chlorine at a sufficiently high temperature to volatilize the chloride. Magnesium chloride, which is also attacked by water, may be protected by adding ammonium chloride. On evaporating a solution containing these two chlorides a residue is left, from which the latter may be expelled by heat.

Many of the chlorides are volatile ; three, viz. those of lead, mercury, in the mercurous state, and silver, are insoluble, and all respond to one or other of the tests given below.

The chlorides of gold and platinum are decomposed by heat, and have occasionally been used for making chlorine, but the rest are stable.

Nearly all metallic chlorides evolve hydrochloric acid when warmed with oil of vitriol (141), and evolve chlorine if warmed with sulphuric acid and a peroxide (Expt. 107). They give red fumes of oxychloride of chromium (CrO_2Cl_2), if distilled with strong sulphuric acid and a bichromate.

The chlorides of the non-metals are apt to react with water, and with compounds containing hydroxyl. Thus phosphorus pentachloride gives the oxychloride (POCl_3) and phosphoric acid :—



Double chlorides. The chlorides of gold and platinum readily enter into combination with chloride of potassium, or with chloride of ammonium, forming double salts (see 557, 558).

Perchlorides. See 447.

147. Action of chlorine with cold alkalis. EXPERIMENT 118. **Action of chlorine on a cold solution of potassium hydroxide.** Pass a stream of chlorine through some solution of potassium hydroxide in a flask cooled by immersion in cold water. When the absorption of chlorine seems to be complete, add a few drops more potash and examine the product. You will find —

(a) That the liquid thus obtained has not the odour of chlorine, but rather a smell resembling that of ‘chloride of lime.’

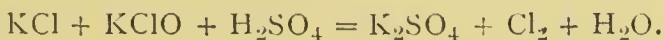
(b) That it gives a precipitate with silver nitrate which is insoluble in nitric acid. Therefore a chloride is present.

(c) That when you add a few drops of sulphuric acid to the solution, it gives off chlorine plentifully.

Now we have seen that in order to liberate chlorine from a chloride by means of an acid, an oxidizing agent must be added. This fact, together with the results of experiments *b* and *c*, suggests that the cold alkali and chlorine have produced potassium chloride and an oxidizing agent. The oxidizing agent in question has been found to be the potassium salt of hypochlorous acid (HClO), formed according to the following equation :—

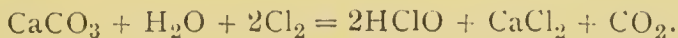


The solution obtained in the above experiment is known as 'bleaching solution,' but it is not of itself an active bleaching agent, as may be proved by immersing a strip of Turkey red twill in it. If an acid be added to it, chlorine is set free :—



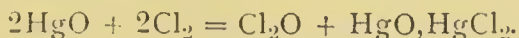
It can therefore be used in conjunction with an acid for bleaching and disinfecting purposes.

148. Hypochlorous acid (HClO). This is formed when a stream of chlorine is passed into water holding calcium carbonate in suspension :—



The solution thus made possesses a somewhat chlorine-like smell, and slowly decomposes, if it be strong, producing chloric acid (HClO₃), free chlorine, oxygen and water. It is a powerful oxidizing agent.

149. Hypochlorous anhydride or chlorine monoxide (Cl₂O). This is a yellow gas, which is formed when chlorine is passed over well cooled mercuric oxide :—



It is apt to explode on a slight elevation of temperature. When cooled it readily condenses to a liquid. With ice-cold water it forms hypochlorous acid (HClO), and a dilute solution containing this acid may be made by agitating well cooled chlorine water with mercuric oxide.

150. Bleaching powder. EXPERIMENT 119. The preparation and properties of bleaching powder. **Synonym :** chloride of

lime. Place some broken glass and then a layer of carefully slaked lime (CaH_2O_2), free from lumps, in a funnel, and pass a slow current of chlorine up the neck of the funnel. After a few hours the lime will acquire a faintly chlorous odour, and become much more soluble than slaked lime; it will then give off chlorine if a mineral acid is added to it. This last quality makes bleaching powder useful as a source of chlorine.

EXPERIMENT 120. The uses of bleaching powder. Bleaching by means of bleaching powder. Shake up about 20 grams of bleaching powder with half a litre of water, and decant the clear solution. Prepare also some dilute hydrochloric acid. Dip a piece of Turkey red twill in the bleaching solution, wring it out, and then dip it in the acid. After a few seconds withdraw the cloth from the acid, wring it out as before, and wash it with water. Then dip it again in the bleaching solution, then in the acid, and so on, until its colour is destroyed. When the acid and the bleaching solution meet in the fibres of the cloth, chlorine is, of course, liberated, and by proceeding in the manner described, the amount of chlorine wasted is reduced to a minimum, and comparatively little injury is done to the cloth.

Bleaching powder as a disinfectant. When bleaching powder is exposed to atmospheric air, it is said to be slowly decomposed by the carbon dioxide present. It is probable that its power as a disinfectant depends on this action.

Finding the value of bleaching powder. The value of bleaching powder does not depend upon the amount of chlorine it contains, but upon the amount of free chlorine we can obtain from it. The maximum proportion of this 'available chlorine' is about 36 per cent. It may be measured by the volumetric process given in Expt. 155, 4.

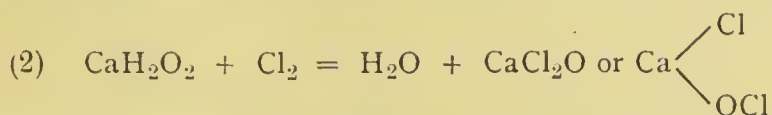
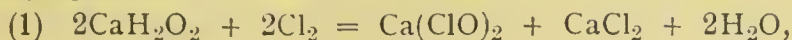
EXPERIMENT 121. To study the oxidizing power of bleaching powder. Dissolve some lead nitrate and manganese sulphate separately in water.

1. Add to the solutions some solution of sodium hydroxide. The lead salt will give a colourless precipitate of its hydroxide. The manganese salt will give a pale-coloured precipitate of manganous hydroxide which rapidly becomes dark in air.

2. Add solution of bleaching powder, in excess, to other portions of the same solutions and warm them. You will now obtain the puce-coloured peroxide of lead (PbO_2) and peroxide of manganese (MnO_2).

The composition and constitution of bleaching powder. Bleaching powder is believed to contain a chloride together with a

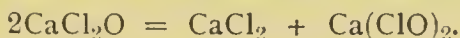
hypochlorite, which may be formed according to one or other of the following equations:—



When a solution of bleaching powder in water is evaporated *in vacuo*, it yields crystals, corresponding to the formula $\text{Ca}(\text{ClO})_2$, and the mother liquor contains much calcium chloride.

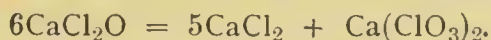
Again, if a solution of bleaching powder be dialyzed (309), the proportion of oxidizer which passes into the diffusate is less in proportion to the chloride than that which remains in the undiffused part. It is therefore probable that an aqueous solution of bleaching powder contains a mixture of calcium hypochlorite ($\text{Ca}(\text{ClO})_2$) and calcium chloride (CaCl_2) (equation 1).

On the other hand, if some fresh and well-made bleaching powder be shaken with alcohol, the latter leaves very little residue when it is separated from the residual solid and evaporated. But calcium chloride (CaCl_2) is freely soluble in alcohol, and therefore there cannot be much of this salt in dry bleaching powder as alcohol does not extract it. This last fact, which is inconsistent with the truth of equation 1, suggests that 2 is more likely to be correct; and that when bleaching powder is dissolved in water, the compound $\text{Ca} \begin{array}{l} \text{Cl} \\ \text{ClO} \end{array}$ decomposes into the two salts which can be obtained from its solution, thus:—



These conclusions are confirmed by the fact that fresh, well-made bleaching powder is less deliquescent than we should expect it to be, if it contained a large proportion of calcium chloride.

The composition of bleaching powder does not correspond exactly to the formula CaCl_2O . It always contains excess of calcium hydroxide. and if the lime be allowed to become hot during the process of manufacture, or if the bleaching powder be heated afterwards, it may also contain some calcium chlorate ($\text{Ca}(\text{ClO}_3)_2$), which may be supposed to be formed according to the following equation:—



151. The action of chlorine on hot alkalis. It was mentioned in the last paragraph, that if the temperature of the slaked lime is

allowed to rise during the manufacture of bleaching powder some calcium chlorate ($\text{Ca}(\text{ClO}_3)_2$) will be formed.

EXPERIMENT 122. To make potassium chlorate. This salt may be made by passing chlorine into a strong and warm solution of potash, when the chlorate and chloride of potassium are produced :—



If the product of the operation be cooled, crystals of potassium chlorate will form. These should be recrystallized from hot water to remove adherent chloride.

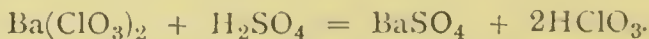
Owing to its richness in oxygen and to the readiness with which it is reduced, potassium chlorate is extensively used in the manufacture of fireworks, lucifer matches, &c. For its behaviour when heated see 117.

In making potassium chlorate on the large scale, milk of lime* is treated with chlorine at 65° to 70° , care being taken to avoid over-heating, for if that occurs oxygen is evolved at the expense of the chlorate. The proportion of chlorate present in the solution is then ascertained, a calculated quantity of potassium chloride added, the liquid concentrated and left to cool, when potassium chlorate is deposited and the highly soluble calcium chloride left in solution.

Chlorate of potassium is also made by the electrolysis of an aqueous solution of the chloride.

152. Chloric acid. **EXPERIMENT 123. To prepare an instable acid such as chloric acid.** When a chlorate is treated with strong sulphuric acid, chloric acid (HClO_3) may be liberated in the first instance, but if so it undergoes very rapid change (see below). Chloric acid, and other instable acids, may be obtained, in solution, by such a process as that which follows :—

Dissolve a known weight of barium chlorate ($\text{Ba}(\text{ClO}_3)_2$) in water and add gradually an equivalent proportion of sulphuric acid diluted with water :—



Allow the insoluble barium sulphate (BaSO_4) to subside, decant the acid solution, and concentrate it over sulphuric acid *in vacuo*.

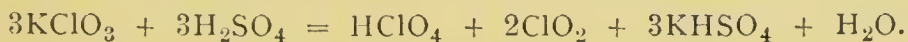
Chloric acid exhibits an acid reaction and a chlorine-like smell. Like

* That is, slaked lime suspended in water.

other similar compounds containing chlorine and oxygen, chloric acid is a powerful oxidizing and bleaching substance; when gently heated it changes into perchloric acid (HClO_4), oxygen and chlorine being evolved (see 154).

153. Perchloric acid (HClO_4). 1. When chloric acid is heated, it is resolved into perchloric acid together with free oxygen and chlorine.

2. If chlorate of potassium, or some other chlorate, be cautiously warmed with strong sulphuric acid *in very small quantities at a time*, a violently explosive gas, chlorine peroxide (154), is evolved, and free perchloric acid mixed with the acid sulphate of potassium is left:—



3. The potassium salt of perchloric acid is one of the products of the action of heat on potassium chlorate (117). The acid may be prepared from this salt by distilling it with strong sulphuric acid. Perchloric acid, when strong, forms an oily, very dense fuming liquid, which, though more stable than chloric acid, is a powerful oxidizer and is said to be highly destructive of organic substances. Most of its salts are very soluble.

Mix a very little chlorate of potassium with some powdered sugar, add a drop of sulphuric acid cautiously to liberate the acid of the salt. Make a similar experiment, using potassium perchlorate in place of chlorate.

The result will show you that the oxidizing power of perchloric acid is far less than that of chloric acid, although the former contains more oxygen than the latter.

154. Chlorine peroxide (ClO_2). It is not desirable that a young student should meddle much with highly explosive substances. He may, however, make Experiment 124 *under supervision*.

EXPERIMENT 124. **The preparation and some properties of chlorine peroxide.** 1. Place one crystal of chlorate of potassium in a test tube, and add a drop of strong sulphuric acid. Notice that the liquid darkens, and that a pale yellow gas is evolved, with an odour much like that of chlorine. This gas is chlorine peroxide (ClO_2), formed as explained above. Turn the mouth of the test tube towards the wall, and warm the glass cautiously. A violent explosion or succession

of explosions will occur owing to the decomposition of the oxide of chlorine.

The gas is readily absorbed by alkalis, and is a powerful oxidizing and bleaching agent.

2. Place 5 or 10 grams of potassium chlorate, in crystals, together with a *few very small* fragments of phosphorus, at the bottom of a good-sized beaker filled with water and standing on a plate. Then cautiously pour a little strong sulphuric acid to the bottom of the beaker by means of a thistle funnel. As soon as this is done the phosphorus will ignite and undergo vivid combustion beneath the water.

Exercise for the student. Write a short essay showing that as a rule the most stable of the oxyacids of chlorine are those which contain the largest proportion of oxygen.

155. The oxides and oxyacids of the halogens. A few of the following acids are best known by their salts:—

OXIDES.

Chlorous oxide or Chlorine monoxide	Cl_2O .
Chlorine peroxide	ClO_2 .
Iodine pentoxide	I_2O_5 .

No oxide of bromine or fluorine has yet been prepared.

ACIDS.

Hypochlorous acid	HClO
Chlorous acid (?) .	HClO_2
Chloric acid . . .	HClO_3
Perchloric acid . .	HClO_4
Hypobromous acid	HBrO
Bromic acid . . .	HBrO_3
Hypoiodous acid .	HIO
Iodic acid . . .	HIO_3
Periodic acid . .	HIO_4

CORRESPONDING SALTS.

Hypochlorites, e.g.	KClO
Chlorites „	KClO_2
Chlorates „	KClO_3
Perchlorates „	KClO_4
Hypobromites „	KBrO
Bromates „	KBrO_3
Hypoiodites „	KIO
Iodates „	KIO_3
Periodates	p. 219.

BROMINE (Br_2): Atomic weight, 79.36.

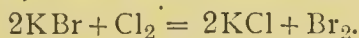
156. This element was discovered, in 1826, by Balard, who obtained it from bittern, the liquid which remains after most of the salt has been removed from sea-water. It occurs in the waters of mineral springs at

Woodhall Spa, and elsewhere, usually in combination with magnesium or calcium, but never free. Bromine is also found, together with iodine, chlorine, &c., in kelp (163).

Most of our bromine comes from certain salt springs in America, and from the deposits of carnallite at Stassfurt; some is made from kelp.

EXPERIMENT 125. To obtain bromine from a bromide.

1. Place a few drops of solution of bromide of potassium in a test tube, and add a drop or two of chlorine water. The liberated bromine may be recognized in the solution by its yellow colour and its odour. Bromine is largely obtained by treating the mother liquors in salt factories with chlorine :—



The liberated bromine is carried off by steam and condensed.

2. Place three parts of potassium bromide, mixed with one of manganese dioxide, in a small flask *A* (Fig. 67). Add about four parts of strong sulphuric acid* diluted with two of water through

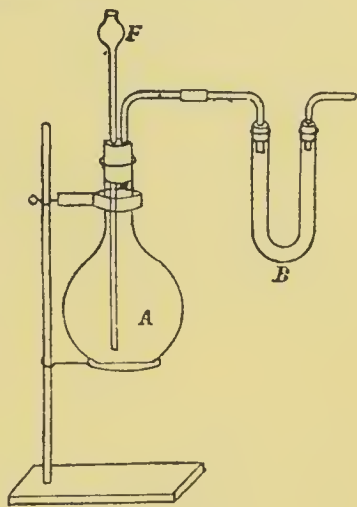
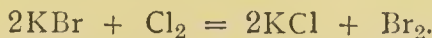


Fig. 67.

F, and warm the mixture gently. Bromine will be liberated, and may be condensed in *B*, which must be well cooled :—



Crude bromine is apt to contain chlorine, which may be removed by digesting it with potassium bromide. This removes the chlorine, and the purified bromine can then be recovered by distilling it :—



To remove iodine, the bromine is distilled from zinc oxide.

Bromine boils at 63° and freezes at -7° . If a sealed tube containing bromine is strongly heated, the bromine becomes opaque, and like dark resin in appearance. At 220° its density is about 80 ($H=1$), but

* The quantities mentioned are only approximately correct. They are calculated from the equation given below. The student should accustom himself to weigh and measure the materials for his experiments, and not work in a haphazard fashion.

it diminishes at higher temperatures. From this it is supposed that at high temperatures its molecules dissociate:—



EXPERIMENT 126. Some properties of free bromine. 1. Notice the offensive odour of bromine, taking care not to expose the eyes to the vapour, and only to smell it when freely diluted with air.

2. Place a cork in a bottle containing bromine, and observe that the cork is rapidly destroyed.

3. Put a drop of bromine in some water. Notice that it sinks ($D = 3.19$), partly dissolving and giving a yellow solution.

4. Cool some bromine water to 4° . Crystals, having the composition $\text{Br}_2 \cdot 10\text{H}_2\text{O}$?, will form.

5. Add a drop of bromine water to solution of iodide of potassium containing starch. Iodine will be liberated and form blue iodide of starch:—



6. Pass hydrogen through a U tube containing fragments of pumice stone soaked with bromine, and provided with a jet; ignite the mixture which escapes. Clouds of dense colourless acid fumes, resembling those of damp hydrogen chloride, will testify to the formation of an acid fuming gas. This is hydrogen bromide (HBr).

7. Place some Dutch gold in bromine. The metal will combine with the bromine, but much less readily than with chlorine.

8. Place a strip of Turkey red twill in some bromine water. It will be bleached much less rapidly than when chlorine is employed.

157. Hydrogen bromide, hydrobromic acid (HBr). We have just seen that this acid is formed by direct union of its elements. Let us try to obtain hydrogen bromide from a metallic bromide, as we obtained hydrogen chloride from sodium chloride (Expt. 115).

Warm a crystal of bromide of potassium with strong sulphuric acid. Notice that colourless fumes are given off, but that they rapidly acquire the colour and odour of bromine. The latter change is due to the reduction of part of the sulphuric acid by hydrogen bromide, for example:—

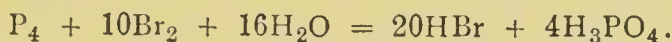


EXPERIMENT 127. The preparation of hydrogen bromide.

1. Warm some potassium bromide with a mixture of one volume of sulphuric acid and two volumes of water. Hydrobromic acid gas nearly free from bromine, but mixed with steam, will be produced.

2. If bromide of phosphorus (PBr_5) be allowed to act on water, hydrogen bromide and phosphoric acid are formed, and a convenient method of making hydrogen bromide has been based upon the reaction. Place some moist red phosphorus in a capacious flask *A* (Fig. 68), and drop ten or twelve times its weight of bromine upon it very gradually from *B* by the tap *T*. The action is rather violent, and dense fumes will be given off which dissolve in the water *D*.

According to the books the following change occurs:—



The reason for using the peculiar form of delivery tube *C* will become manifest when you make the experiment. *E* should contain some red phosphorus to prevent free bromine from reaching *D*.

3. Pass hydrogen sulphide (183) through some bromine water, adding more bromine as the first portions disappear. Filter, or decant, the solution from the sulphur which is deposited, and examine its action with litmus, an alkaline carbonate, chlorine water, manganese dioxide, and with silver nitrate.

You will find that it contains an acid which yields bromine when oxidized and which gives a pale yellow precipitate with silver nitrate. It has been found, by other experiments, to be hydrogen bromide, formed partly according to the following equation:—



Hydrobromic acid made by this process usually contains some sulphuric acid, and if a little solution of barium chloride be added to some of it, a white precipitate of barium sulphate will be formed.

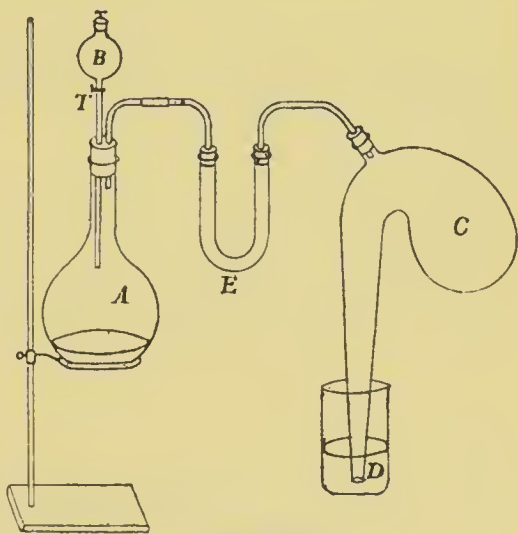


Fig. 68.

Hydrogen bromide, as we have seen from the preceding experiments, is a colourless acid gas which fumes violently in air. It has been condensed to a liquid, which solidifies at -73° . It is decomposed by sodium and potassium, hydrogen being liberated (see HCl, Expt. 116), and also by chlorine. When treated with a peroxide, such as manganese dioxide, it yields free bromine.

A solution of hydrogen bromide can be obtained, which contains 48.2 per cent. of hydrogen bromide, and boils at 126° ; but, as in the case of the similar solution of hydrogen chloride, its boiling-point and composition depend to some extent on the pressure at which it is distilled.

158. Metallic bromides. Most of these salts may be made by methods similar to those employed for preparing chlorides; they are colourless, and most of them are soluble.

Potassium bromide (KBr) is used largely in medicine. It is made by saturating a solution of potassium hydroxide with bromine, and evaporating the product to dryness; the resulting mixture of bromide and bromate of potassium is then ignited alone, or with finely divided carbon, to reduce the bromate.

Many metallic bromides bear a high temperature without decomposing, but those of gold and platinum are easily decomposed, and some others, e.g. copper bromide, evolve bromine when heated in air. When heated with oil of vitriol, they yield, as we have seen, a mixture of hydrogen bromide and free bromine.

Questions to be answered by the student after re-reading the sections on chlorine.

1. How would you collect hydrogen bromide in the state of gas?
2. How would you establish the composition of hydrogen bromide qualitatively and quantitatively (Expt. 116, 117)? Why cannot we employ the electrolytic method?
3. How would you endeavour to prove that hydrogen bromide contains no oxygen?
4. How would you prepare sodium bromide, and silver bromide?
5. How would you find the equivalent weight of bromine?
6. Why do you consider bromine to be an element?
7. Quote evidence to show that bromine is univalent.

159. Some properties of combined bromine. The student should compare the properties of some compounds of bromine with those of elementary bromine.

He has already learnt that all bromides evolve bromine when they are acted on by chlorine, or by acids in the presence of oxidizing agents; and that when heated with strong sulphuric acid, they give off fumes of hydrogen bromide mixed with free bromine. He will find also that, like chlorides, they precipitate solutions containing silver nitrate, but that silver bromide may be distinguished from silver chloride by the yellow colour of the former compound.

160. Chlorine and bromine. These elements readily combine to form a volatile liquid, which has the formula ClBr .

161. Oxyacids of bromine. No oxides of bromine have been prepared.

EXPERIMENT 128. Hypobromous acid (HBrO). Shake some bromine water with a little precipitated mercuric oxide. Notice that the colour and odour of the bromine disappear, and that the solution acquires an aromatic, pepper-like odour, which resembles that of hypochlorous acid. Examine the action of the solution as a bleaching agent; and ascertain whether it yields bromine when a mineral acid is added to it.

Exercises for the student. These should be done after consulting the references.

1. Give an equation to account for the production of hypobromous acid (see 149).

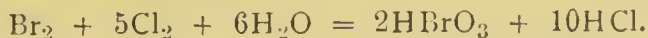
2. Explain how chloride of bromine would be likely to act on an alkali (see Expts. 118 and 122).

3. Add bromine gradually to a cold solution of an alkali. Notice that as before the bromine is destroyed.

Examine the behaviour of the solution with acids, and try its action on a solution of lead nitrate (Expt. 121). You will find it resembles the solution prepared in a similar manner from chlorine. We may therefore suppose that it contains a hypobromite and a bromide:—



162. Bromic acid and the bromates. 1. When chlorine gas is passed through bromine water, bromic acid (HBrO_3) and hydrogen chloride (HCl) are formed*:—



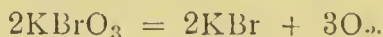
* It follows that when testing for combined bromine with chlorine we must avoid using excess of chlorine.

2. If bromine be added to a hot solution of an alkali, the bromate and bromide of the metal of the alkali will be produced (compare Expt. 122):—



But as five-sixths of the bromine are wasted when a bromate is prepared in this way [why?], it is better to saturate a hot solution of an alkaline carbonate with chlorine, and then to add sufficient bromine to decompose the chlorate previously formed. (Note that here bromine replaces chlorine.) The solution will then give a precipitate of silver bromate if suitably treated.

Bromic acid (HBrO_3) has a strongly acid reaction. It bleaches, and is easily decomposed by heat. The bromates, like the chlorates, are most of them soluble, when heated they do not yield perbromates, but are resolved directly into bromides and oxygen:—



IODINE (I_2): Atomic weight, 125.9.

163. Iodine was discovered by Courtois, in 1811, in kelp. It is never found free in nature, but its compounds are widely distributed. Sea-water contains about four parts of an iodate in one million parts, and some seaweeds assimilate this iodine, consequently their ashes, *kelp*, have been an important source of the element. The dried stems of driftweed, *Laminaria digitata*, contain nearly 0.5 per cent. of iodine, but

the common *Fucus vesiculosus* contains much less. Iodine is also found in sea sponges, oysters, herrings, &c., and a great deal is obtained from crude Chili saltpetre, *caliche*, which contains an iodate.

EXPERIMENT 129. To prepare iodine from an iodide. 1. Pass chlorine cautiously through a little strong solution of iodide

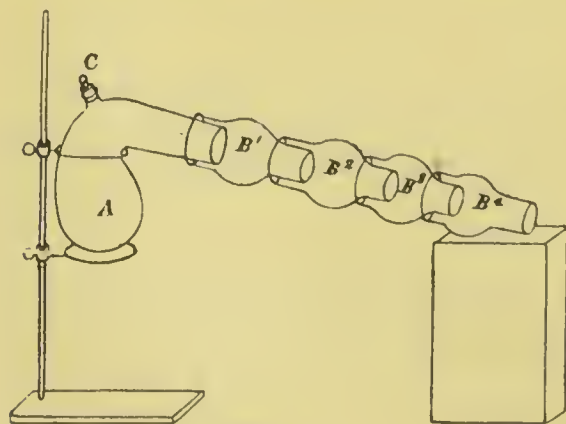


Fig. 69.

of potassium. Notice that the iodide first turns dark brown, and then deposits a dark solid. Collect this on a filter, dry it, and heat it in

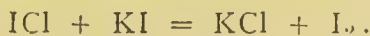
a test tube. It will volatilize, yielding a fine purple or violet vapour, which recondenses in glittering crystals on the cooler parts of the tube.

2. Iodine may be prepared conveniently in the following manner :— Mix four parts of iodide of potassium (KI) with about one part of black oxide of manganese, place the mixture in *A* (Fig. 69); add five parts of sulphuric acid, diluted with two of water, close *C* and heat *A*. Iodine will be given off, and will condense in the aludels* *B*¹*B*²*B*³*B*⁴. The reaction may be expressed as follows :—



164. Manufacture of iodine. To extract iodine from kelp, the kelp is lixiviated with water to separate the soluble salts from the charcoal. The solution thus obtained is evaporated, and deposits potassium sulphate (K_2SO_4) as the concentration proceeds. It is subsequently cooled, that potassium chloride, &c. may separate. The concentrated liquor is mixed with oil of vitriol, which precipitates sulphur, owing to the decomposition of sulphides and thio-sulphates. The acid liquor, which still contains iodides, bromides, and chlorides, is transferred to retorts provided with condensers. Manganese dioxide is added gradually in proper proportion, and the iodine is distilled off. When all the iodine has been obtained, more manganese dioxide is added to liberate the bromine.

The iodine made in this way is very apt to contain chlorine and bromine, and it sometimes contains a dangerous substance, called iodide of cyanogen (ICN). These may be removed by redistilling the iodine with iodide of potassium, when the iodine sublimes and the bromine and chlorine are fixed in the form of potassium salts. If ICl be present, the following reaction will occur :—



The iodine in *caliche* occurs as sodium iodate. It cannot be set free by the above method, but can be liberated by reducing agents.

Add chlorine water to a little solution of iodate of potassium. No iodine will be liberated.

Add a little solution of sulphur dioxide to a fresh portion of the iodate. You will easily obtain free iodine.

In Chili the mother liquors from the nitre are treated with a bisulphite, which precipitates the iodine in the solid form. It is then collected and sublimed.

* Small lamp glasses make good aludels.

165. Properties of iodine. EXPERIMENT 130. Some properties of elemental iodine. 1. Heat a few crystals of iodine in a dry flask. Notice that its vapour at first exhibits a reddish tinge, but subsequently, when more dense, becomes purple and at length violet when seen by transmitted light. If the light transmitted by iodine be examined with a small spectroscope (336), it will be found that first the green rays disappear, and that afterwards, as the vapour becomes more dense, the red rays are absorbed. It is at this last stage that iodine vapour appears blue or violet to the eye.

The melting-point of iodine is 114° . It volatilizes slightly at ordinary temperatures, as may be recognized by its faint chlorine-like smell. Below 700° iodine ($D = 126.0$) forms the heaviest vapour known, but at higher temperatures its density decreases. This may be explained by supposing that the molecules of iodine dissociate. (See also bromine.) Thus :—



2. Add a very minute particle of iodine to some carbon disulphide or chloroform. It will dissolve, and the solution will exhibit colours similar to those of its vapour.

3. Add a fragment of iodine to some alcohol. It will form a brown solution.

4. Shake some finely powdered iodine with water. You will find that it dissolves very sparingly indeed.

5. Add some iodine to a solution of potassium iodide. It will dissolve freely, giving a deep brown solution*, which will stain the skin.

It has been suggested that the different colours of these solutions may be due to differences in the complexity of their molecules. If a solution of iodine in carbon disulphide be cooled by a freezing mixture of ether and carbon dioxide, it becomes brown, which suggests that the brown solutions may contain the more complex molecules. On the other hand, crystals of a periodide corresponding to the formula KI_2 or KI_3 have been obtained from concentrated solutions of iodine in potassium iodide, so that the solvent power of iodides may be connected with the forming of such a periodide.

6. Add a little freshly made starch solution to a solution of iodine in water containing potassium iodide, a fine blue coloration will be

* A very strong solution of impure iodine in iodide of potassium deposits crystals of pure iodine if it be diluted.

produced. Heat the blue liquid to 85° ; its colour will disappear. Cool the solution again; it will again become blue. The exact nature of the blue substance thus formed is not understood. It is sometimes described as a 'lake.' It appears to consist of iodine and starch, but it is sometimes difficult to produce it by the mere addition of iodine to a solution of starch. So intense is its colour, that it is said one part of iodine in 450,000 parts of solution may be detected by the above test.

7. If hydrogen be passed over iodine in daylight, no sign of combination will be observed; but if hydrogen, together with iodine vapour, be passed through a red-hot tube, an acid fuming gas (HI) is produced.

8. Rub together five parts of iodine and four parts of mercury, moistened with spirit, in a mortar. A reddish powder, mercuric iodide (HgI_2), will form.

9. Warm some fragments of iodine with some clean iron filings and a little water in a flask. When the colour of the iodine has disappeared, decant the solution, and evaporate a few drops of it. It will leave a residue which possesses the chalybeate flavour of a salt of iron. Test some of the solution for iron (see 499), also for iodine: both will be found to be present.

The results of the last two experiments show that, although iodine has but little affinity for hydrogen, it unites readily with metals.

EXPERIMENT 131. Some properties of combined iodine. 1. Add some solution of starch to a compound of iodine. No blue iodide of starch will be formed.

2. Compare the smell, volatility, &c., of several compounds of iodine, with those of the element in the free state.

3. Pass a bubble of chlorine through a solution of a soluble iodide. Iodine will be liberated:—



4. Warm an iodide with strong sulphuric acid and an oxidizing agent. Iodine will be given off.

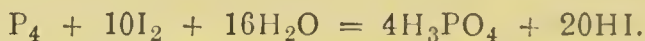
5. Add some solution of silver nitrate to a solution of a soluble iodide. A yellow precipitate of silver iodide (AgI) will form.

6. Repeat experiments 1, 3 and 5, using a compound containing oxygen, e.g. potassium iodate. The results will be negative. Add a little solution of sulphur dioxide to the substance. Iodine will be liberated, and may be recognized by the usual tests.

166. Hydrogen iodide or Hydriodic acid (HI). EXPERIMENT 132. **Methods of preparing hydrogen iodide.** 1. Hydrogen and iodine combine directly at a red heat, especially in the presence of spongy platinum.

When strong sulphuric acid is added to an iodide, it does not evolve hydrogen iodide (HI), but a mixture of this substance, together with free iodine and products of the reduction of the sulphuric acid.

2. Place about 1 part of red phosphorus mixed with 20 parts of iodine in a flask provided with a very capacious delivery tube (see Fig. 68), and drop upon it gradually about 3 parts of water. When the action is complete, apply heat and collect the gas in solution in water. The equation for the above change is usually represented as follows :—



Crystals of phosphonium iodide (PH_4I) are sometimes formed as a by-product (see 252).

3. Pass a stream of hydrogen sulphide through some water holding finely powdered iodine in suspension. A little hydrogen iodide will soon be formed, and this will dissolve some more iodine, which will be converted, in its turn, into hydrogen iodide :—



Then yet more iodine will be dissolved and converted into iodide, until a strong colourless solution of iodide of hydrogen containing suspended sulphur will be formed. When a fair amount of iodine has been dissolved, let the sulphur settle, and decant the solution.

This method of preparing hydriodic acid yields a fairly strong solution, which is free from sulphuric acid, but the action ceases when the liquid contains 48 per cent. of the acid.

EXPERIMENT 133. **The properties of solution of hydrogen iodide.** 1. Examine the action of the solution on litmus.

2. Neutralize some of it with sodium hydroxide, and evaporate the solution. You will get colourless, cubical crystals of sodium iodide (NaI).

3. Expose a little of the solution to the air. Iodine will soon be liberated and will give a brownish colour to the solution.

4. Warm some solution of hydrogen iodide with peroxide of manganese, or with peroxide of lead. The halogen will be liberated :—



Hydrogen iodide is a heavy gas which, like hydrogen chloride, fumes vigorously in moist air. A hot platinum wire dipped into the

gas easily effects its decomposition. Owing to the readiness with which it is decomposed it is a useful reducing agent.

Questions for the student.

1. How would you collect and analyse hydriodic acid gas (157)?
2. What would you expect to see if you decomposed a solution of hydrogen iodide by a current of electricity?
3. How do you suppose cyanogen iodide (ICN) would react with a solution of potash (KHO)?
4. Warm some potassium iodide with strong sulphuric acid. Observe the result. Read what is said about the action of potassium bromide and strong sulphuric acid (157), and explain what has happened to the iodide.

167. The metallic iodides. Iodide of potassium, which is largely used in medicine, may be obtained by neutralizing hydrogen iodide with potassium hydroxide or carbonate, but it is more conveniently made by adding iodine to potash, whereby a mixture of iodate and iodide of potassium is formed:—



This is ignited with finely powdered carbon to reduce the iodate, and recrystallized from water (compare KBr, 158).

The iodides of lead, mercury, and silver exhibit characteristic colours, and are insoluble.

EXPERIMENT 134. To make the iodides of lead, mercury, and silver. Lead iodide. Mix about 3 grams of iodide of potassium, dissolved in water, with a solution containing 3 grams of nitrate of lead; collect and wash the precipitated iodide of lead:—



Then heat the precipitate with some water in a flask. It will gradually dissolve (compare lead chloride, 446), and on cooling will crystallize in brilliant golden-yellow scales.

Mercuric iodide. Mix solutions containing equivalent weights of potassium iodide (KI) and mercuric chloride (HgCl_2). A scarlet precipitate of mercuric iodide will fall:—



Divide the liquid and precipitate into three parts.

(a) Add more solution of potassium iodide to one portion. The iodide of mercury will dissolve, owing, it is believed, to the forming of a double salt.

(b) To a second portion add more solution of mercuric chloride. The red iodide will again dissolve, forming a colourless solution.

(c) Collect and dry the remainder of the mercuric iodide, and heat it in an ignition tube. It will melt and boil, yielding a fine yellow sublimate which, especially if it be disturbed, will change into beautiful red crystals on cooling.

Copper iodide. As copper is divalent, we might expect it to form a cupric iodide (CuI_2).

Mix solutions containing equivalent proportions of copper sulphate and iodide of potassium, and collect the drab-coloured precipitate which falls. You will easily detect iodine and copper in this precipitate.

Examine also the odour and appearance of the filtrate; add a little solution of starch to some of it, and heat a portion to the boiling-point. You will find that it contains a good deal of free iodine, which shows us that the copper salt and the iodide do not react in accordance with the following equation, as we should have expected:—



A fuller examination of the products of this reaction would show that cuprous iodide (Cu_2I_2) and free iodine are formed:—



If a ferrous salt be present when the solutions of cupric sulphate and an iodide are mixed, the former is oxidized to a ferric salt, and all the iodine combines with copper to form cuprous iodide. Try this experiment, and endeavour to express the result obtained by means of an equation.

Silver iodide. Add some solution of silver nitrate to a solution of a soluble iodide; a yellow precipitate of silver iodide (AgI) will fall. Pour nitric acid upon some of it, it will prove to be insoluble like chloride of silver.

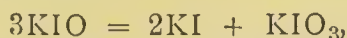
168. Oxides and oxyacids of iodine. EXPERIMENT 135. **Hypoiodous acid (HIO).** Add iodine to a cold solution of potash in the proportion of about 127 parts of iodine to 56 parts of potassium hydroxide.

Repeat the experiment adding some rectified spirit. Notice that it acquires a peculiar odour, and deposits a yellow crystalline substance on cooling. This substance is iodoform (CHI_3).

Boil the other portion, and afterwards warm it with alcohol. No iodoform will be produced.

Therefore it is evident that iodine, like chlorine, reacts differently with hot and cold alkali. And since it is known that a hypochlorite

gives chloroform (CHCl_3) when it is treated with alcohol, it seems likely that the power possessed by cold iodized potash of giving the corresponding iodine compound (CHI_3), indicates the presence of a hypiodite in the iodized solution. Hypiodites, however, change so rapidly into iodate and iodide :—



that the former salts have not been isolated.

169. Iodic anhydride (I_2O_5), iodic acid, and iodates.

Heat some iodic acid by an oil bath to 170° . Water will be given off, and iodic anhydride, or iodine pentoxide, will be left. At 130° an intermediate compound (HIO_3 , I_2O_5) is formed.

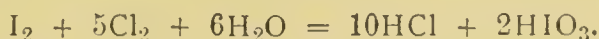
Heat more strongly a little iodic anhydride in a tube. Notice that iodine is liberated, and test the contents of the tube for oxygen.

Iodic acid. We have already learnt that iodates occur in sea-water and in Chili saltpetre, and that they are formed when alkaline hydroxides are treated with iodine.

EXPERIMENT 136. To make iodic acid.

1. Heat 1 part of iodine with 2 of nitric acid in a flask provided with an inverted condenser (Fig. 70) in order that the vapours of the acid and the iodine may be condensed and flow back into the flask. Renew the acid at intervals, until the iodine is destroyed, and evaporate the solution obtained cautiously. Crystals of iodic acid will remain.

2. Pass a stream of chlorine through a mixture of 20 parts of water with 1 of finely powdered iodine. The iodine will be gradually oxidized, hydrochloric acid and iodic acid being produced :—



Properties of iodic acid. Iodic acid crystallizes in six-sided colourless plates, which are very soluble in water, and form an acid solution, which possesses bleaching power.

Add some solution of starch to a little iodic acid. The starch will remain unaffected. Add a little sulphurous acid, avoiding excess. Iodine will be liberated.

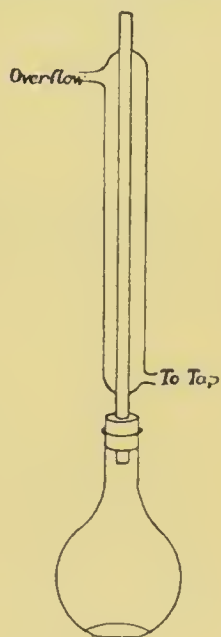
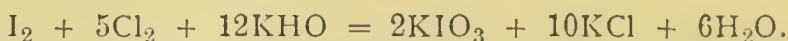


Fig. 70.

Iodates. Potassium iodate is formed, together with potassium iodide, when iodine is dissolved in potassium hydroxide (see 167). A more economical method of making the salt might be to treat the alkali with iodine and chlorine in suitable proportions, as suggested by the following equation:—



It may also be made from potassium chlorate by warming 2.6 parts of potassium chlorate dissolved in about 50 parts of water, with 3 parts of powdered iodine, and 2 c.c. of nitric acid containing 20 per cent. of acid. When the iodine has disappeared the product is boiled and then gently evaporated; the residue consists of potassium iodate together with some iodide. In this experiment the iodine may be supposed to replace the chlorine:—



Question for the student. It has been shown that iodine and bromine are displaced from their salts by chlorine. Give examples to show that the reverse of this is true in the case of compounds which contain oxygen.

Iodic acid, like chloric acid and bromic acid, is *monobasic* (see 114). Therefore the above salt (KIO_3) is the normal iodate, and no acid salts should exist, but the alkaline iodates have a notable power of combining with the parent acid, producing such salts as potassium di-iodate ($\text{KIO}_3, \text{HIO}_3$) and potassium tri-iodate ($\text{KIO}_3, 2\text{HIO}_3$).

Periodic acid (HIO_4 , or $\text{HIO}_4, 2\text{H}_2\text{O}$), and the **periodates**. When an alkaline iodate is heated it does not yield an alkaline periodate, but is converted directly into an iodide and free oxygen.

To obtain a periodate, chlorine is passed into a hot solution containing sodium hydroxide and sodium iodate in equal proportions. The solution is concentrated and the deposited periodate dissolved in dilute nitric acid. Silver nitrate is added to the acid solution thus obtained, and the precipitate of silver periodate, which falls, is decomposed by bromine in the presence of water. The bromine throws down a precipitate of silver bromide, leaving periodic acid (H_5IO_6) in solution, together with some bromic acid.

Solid periodic acid (H_5IO_6 or $\text{HIO}_4, 2\text{H}_2\text{O}$) occurs in colourless crystals which melt at 133° . If strongly heated, they are decomposed, yielding water, oxygen and iodine pentoxide. The acid is reduced by sulphur dioxide and other reducing agents. A good many periodates have been prepared. These salts form a somewhat com-

plicated set of compounds, which may be supposed to be derivatives of one or other of the following acids, the third of which alone has been isolated.

Metaperiodic acid	. .	HIO_4
Mesoperiodic	„ . .	$\text{H}_3\text{IO}_5(\text{HIO}_4, \text{H}_2\text{O})$
Paraperiodic	„ . .	$\text{H}_5\text{IO}_6(\text{HIO}_4, 2\text{H}_2\text{O})$
Diperiodic	„ . .	$\text{H}_4\text{I}_2\text{O}_9(2\text{HIO}_4, \text{H}_2\text{O})$

170. Compounds of iodine with the other halogens.

Iodine monochloride (ICl). When chlorine is passed over iodine until the whole just becomes fluid, a reddish-brown liquid is formed, which slowly crystallizes. This is iodine monochloride, which boils at 101° . It reacts with water, producing iodic acid, hydrochloric acid, and free iodine.

Iodine trichloride (ICl_3). This may be made by gently heating iodine in excess of chlorine. It forms long orange-yellow coloured needles, which melt at a low temperature giving off chlorine.

Similar compounds containing bromine are supposed to exist, and there is a pentafluoride of iodine (IF_5).

FLUORINE (F_2): Atomic weight, 18.9.

171. Fluorspar and hydrofluoric acid. Chemists have long believed that fluorspar, or Derbyshire spar, must contain an element of the halogen type, and though this element was quite unknown in the free state till a few years ago it was, provisionally, named *fluorine*. The grounds for this belief will be gathered from what follows.

EXPERIMENT 137. To study the action of sulphuric acid on fluorspar*. Warm half a gram of finely powdered fluorspar in a small dish of lead or platinum, with a few drops of strong sulphuric acid. An irritating acid gas will be given off which fumes violently, like hydrochloric acid, with ammonia and also in damp air; and a solid residue, which may easily be recognized as calcium sulphate (385), will be left in the dish. By measuring the amount of calcium sulphate given by a known weight of fluorspar, it may be shown that there are 40 parts of calcium and 38 parts of the new element in every 78 parts of fluorspar.

By treating fluorspar with sulphuric acid in vessels of lead, fitted

* This *must* be done in a fume closet.

with leaden delivery tubes, the fuming gas has been obtained and dissolved in water. It then forms a very acid and corrosive liquid; this is a powerful solvent; it attacks silver and copper, on which hydrochloric acid has but little action, and corrodes glass so rapidly that it must be preserved in bottles made of india-rubber. When this acid is neutralized it forms salts which, like the chlorides, give acid fumes when warmed with strong sulphuric acid.

The acid from fluorspar has also been isolated in the gaseous state. At 88° its density is about 10 ($H=1$), so that at this temperature its molecular weight is 20 (see 91). Twenty parts of the acid will yield 42 parts of a sodium salt which contain 23 parts of sodium; therefore, it must contain an atom of hydrogen in each molecule, like hydrogen chloride.

On account of the above facts and of the numerous points of resemblance between this acid and its salts, and hydrochloric acid and the chlorides, it was long supposed that the former must contain an element belonging to the halogen group; and as a molecular proportion of hydrogen fluoride (20 parts) contains one part of hydrogen,

19 was adopted as the atomic weight of fluorine. The following formulae will represent the above-mentioned compounds:—

Fluorspar	CaF_2
Hydrogen fluoride .	HF
Sodium fluoride . .	NaF

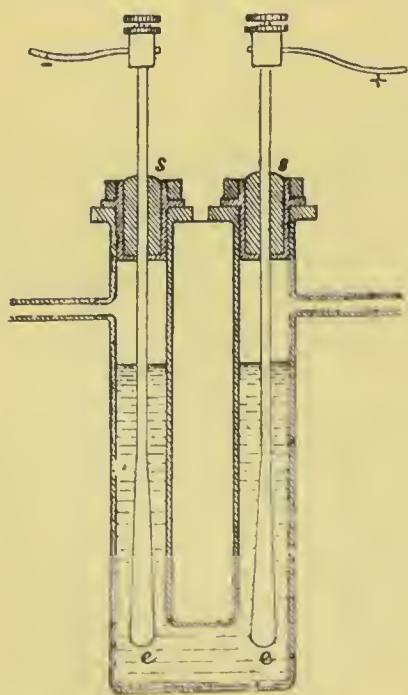


Fig. 71.

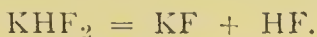
172. The discovery of fluorine by Moissan. Many attempts were made by Davy—who first pointed out the analogy between hydrofluoric acid and hydrochloric acid—Gay-Lussac, and others to isolate fluorine, but all these attempts were without definite success, possibly owing to the fact that free fluorine attacks the materials of the experimental vessels in almost every case.

In 1886 Moissan succeeded in electrolyzing dry hydrogen fluoride, after liquefying it by means of a freezing mixture, and adding about

one-fifth of its weight of hydrogen and potassium fluoride (KHF_2). He used a U tube (Fig. 71) made of platinum*, and closed with fluorspar stoppers *s s* which carried platinum electrodes *e e*.

Moissan found fluorine to be a light greenish-yellow gas, with a pungent odour; it exhibits extraordinary chemical activity, combining violently with hydrogen in the dark, and also with many of the metals, with sulphur, phosphorus, arsenic, antimony, silicon, and boron. It displaces chlorine from chlorides, much as chlorine displaces the other halogens, and decomposes water readily, yielding hydrogen fluoride (HF), and oxygen which is richly ozonized, but it does not appear to unite with oxygen.

173. Hydrogen fluoride and its salts. Gaseous hydrofluoric acid was first made in 1854. It is best prepared by heating the acid fluoride of potassium (KF, HF) in a platinum retort:—



The product must be condensed by a freezing mixture in a platinum receiver. It then forms a liquid which boils at $19\cdot5^\circ$ and is very hygroscopic, like the other hydrogen halides. When dry it is indifferent to glass, but it corrodes that substance rapidly in the presence of moisture, fluorides of silicon (SiF_4) and of the metals being formed; it is therefore useful for etching glass surfaces.

Hydrofluoric acid is extremely unwholesome, and serious accidents have occurred with it, so that only trained chemists may be trusted to use it.

The vapour density of hydrogen fluoride at $26\cdot4^\circ$ is 25.59 ($\text{H} = 1$), but it gradually diminishes, and at 60° to 90° it is only about ten times as great as that of hydrogen†. It was at one time supposed that its molecular formula might be H_2F_2 , but the gradual diminishing of the density of its vapour, with rise of temperature, and the fact that its density becomes nearly constant above 60° , seems to imply that at low temperatures it consists of a mixture of molecules, or of molecular aggregates, of greater complexity than is implied by the formula HF , and that these are gradually resolved by heat into simpler molecules.

The acid exhibits a marked tendency to form double salts of the type $\text{HF}, \text{M}'\text{F}$, by combining with its salts. The action of hydrogen fluoride on glass can be seen by leaving a few drops of the aqueous acid in a test tube, when the bottom of the tube will soon be eaten through; or by sketching a design on a glass plate, coated with wax,

* Copper has been substituted for platinum with success. † Thorpe.

with a sharp steel point, and then rubbing the exposed glass with some cotton-wool soaked in the acid. On washing the glass and removing the wax, the design will be found to be cut into the glass.

174. Metallic fluorides. These are mostly stable. Like fluorspar, they evolve hydrogen fluoride when warmed with strong sulphuric acid (Expt. 137). They are not usually decomposed by heat, but may be converted into oxides if strongly ignited in contact with steam. The fluorides of potassium, ammonium, sodium, and silver are soluble; many others insoluble. Fluorides exhibit a marked tendency to form double salts, such as the potassium salt (KHF_2) previously mentioned, and also to unite with silicon fluoride (SiF_4), forming a class of salts called fluosilicates (175).

175. Silicon fluoride (SiF_4). EXPERIMENT 138. To make silicon fluoride, and study its action on water. Place a mixture of powdered fluorspar and silica (SiO_2), either in the form of flint or of powdered glass, in *A* (Fig. 72), add some strong sulphuric acid, and arrange the apparatus so that *B* reaches almost to the bottom of *D*. Cover the end of *B* with quicksilver at *C*, fill *D* with water, and heat *A*. The fluorspar and sulphuric acid will generate hydrogen fluoride, which will act on the silica and form silicon fluoride :—

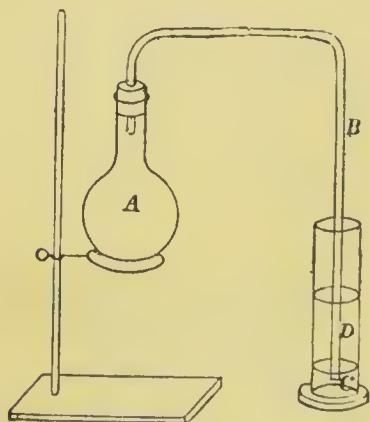
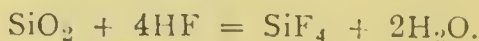


Fig. 72.



Silicon fluoride, as may be learnt by inspecting the contents of *A*, is a colourless gas. It fumes in moist air. As it rises through the water in *D*, a gelatinous deposit of hydrated silica ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) will form, and after some time the liquid in *D* will become acid, owing to the presence of fluosilicic acid (H_2SiF_6) which has been formed simultaneously with the silica :—



Fluosilicic acid is sometimes used as a test for potassium and barium, as the fluosilicates of those metals are somewhat insoluble.

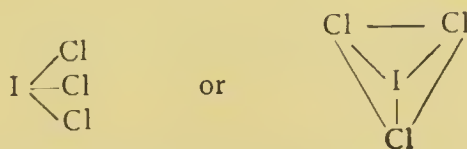
The compounds of fluorine, though not very plentiful, are somewhat widely distributed. It occurs most plentifully in fluorspar, but also in

cryolite (Na_3AlF_6), a double fluoride of sodium and aluminium, found in Greenland; and in other minerals, such as fluor-apatite, in which it is associated with calcium phosphate. Fluorine also occurs in the bodies of animals, and is found in the ashes of many plants. Scheele first recognized hydrofluoric acid in a distinct form of matter in 1771, though it had previously been used for etching glass.

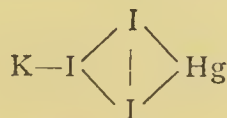
176. Valency of the halogens. It has been stated (104) that since an atom of chlorine will combine with or replace an atom of hydrogen or silver, and no more, to form a molecule of hydrogen chloride or silver chloride, the atom of chlorine is univalent. And what we have learnt about the other halogens will suggest that fluorine, bromine and iodine may also be considered to be univalent. But a closer examination of the properties of these elements makes it difficult to regard all the halogens as univalent; for how could a univalent atom of iodine combine with three univalent atoms of chlorine to form ICl_3 ? How could saturated molecules, corresponding to the formulæ HF and SiF_4 , unite to form fluosilicic acid (H_2SiF_6)? And, again, could the oxide I_2O_5 exist, if iodine were univalent, unless its atoms be arranged in a chain such as the following?—



It therefore seems probable that though these elements are univalent in most compounds, they are capable of exerting a higher valency in some of their combinations (see 104). If we admit that they are trivalent, for example, we may write the formula of iodine trichloride as:—



and that of the double iodide of mercury and potassium as:—

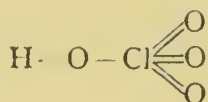


Again, if chlorine be univalent, we must represent perchloric acid (HClO_4) by the formula:—



But if we admit that chlorine may be septemvalent—and its position

in the seventh group under the periodic system of classification suggests that it may be—then the constitutional formula of perchloric acid might be written:—



Exercise for the student. Construct graphic formulæ to explain the constitution of the double salts of fluorine and of iodine, and also of iodine pentoxide, on the assumption that the halogens are trivalent elements.

177. The halogens and the Periodic law. We are now in a better position to grasp the meaning of the statement made in 134, that the ‘properties of atoms are a periodic function of their masses.’

If we arrange the elements in the order of their atomic weights, we shall find that the four halogens are distributed somewhat regularly among the rest (see Group VII, p. 181). These four elements are not by any means exactly alike, but they are all more or less volatile, are all coloured substances, and their vapours all possess pungent characteristic odours. Their vapour densities, and some other physical properties, such as their melting-points and boiling-points, vary with their atomic weights. All form acid hydrides, that of fluorine being most stable, that of iodine least. All unite readily with the metals. Fluorine displaces the other halogens from their compounds with metals; chlorine displaces bromine and iodine, and bromine, in its turn, displaces iodine. All form oxyacids, or salts corresponding to oxyacids, except fluorine, and all these latter compounds are decomposed by heat; those which contain iodine being the most stable.

The above facts afford us a good example of the resemblances and differences which we may look for among the members of any given group of elements under the periodic system of classification. When we have learnt that sulphur is an electro-negative element, whose hydride is slightly acid and highly odorous, and that it forms several acidic oxides, we shall have considerable grounds for expecting to find that selenion, the next member of the same group, is also electro-negative, and also forms a feebly acidic hydride, and one or more acidic oxides. At the same time we must not jump to the conclusion that all the members of every group resemble one another in so marked a manner as the four halogens; for this group has been studied first, partly because its members exhibit so many strong resemblances of a kind likely to be appreciated by a beginner.

CHAPTER XV

SULPHUR. SELENION. TELLURIUM

THESE three elements form a subdivision of the sixth group in the table on p. 181. It will be noticed that oxygen also belongs to this group.

SULPHUR (S_2 ?): Atomic weight, 31.83.

The familiar name of sulphur, brimstone, is derived from *brennstein*, burning-stone.

178. Sources of sulphur. 1. *Native sulphur.* This is found near volcanoes. Our chief supply comes from Sicily, but sulphur mines are also worked on the mainland of Italy, and lately sulphur has been gathered in Japan.

2. *Combined sulphur.* Sulphur compounds are very plentiful. Thus zinc blende (ZnS), iron pyrites (FeS_2), copper pyrites ($Cu_2Fe_2S_4$), and cinnabar (HgS), are examples of important minerals containing sulphur, though, with the exception of iron pyrites, they are chiefly useful as sources of the metals. Hydrogen sulphide is sometimes present in mineral waters, as at Harrogate. The sulphates of barium, calcium, strontium, and magnesium, are well known under the names of heavy spar, gypsum and alabaster, cœlestine, and Epsom salts. Sulphur is also present in the bodies of animals, and small quantities are found in plants; the pungent oils of garlic and horse-radish are examples of substances of vegetable origin containing sulphur.

EXPERIMENT 139. To learn how sulphur behaves when heated. Heat some fragments of sulphur in a retort *A* (Fig. 73). If you examine its behaviour closely, you will observe that it melts below 115° , forming a pale yellow liquid. If you continue to apply heat to this liquid it will darken, and become so viscous that at 220° to 250° the retort may be in-

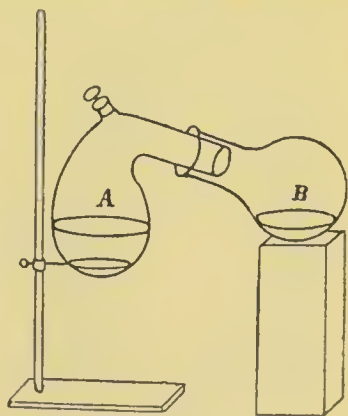


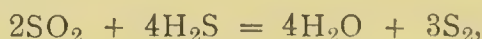
Fig. 73.

verted, for an instant, without its contents being spilt, but as the temperature rises above 250° the sulphur will again lose its vis-

cosity, and become a dark mobile fluid which boils freely at 444.5° and condenses in *B*.

The density of the vapour of sulphur at 500° is about 96, hence its molecular weight at that temperature might be 192, and its formula S_6 . Its density, however, steadily diminishes at higher temperatures, and at 1000° it is 32; thereafter it obeys the laws of Boyle and Charles. As the vapour density of sulphur is not constant over any considerable range of temperature below 1000° , it is doubtful whether a given mass of sulphur ever exists in the form of molecules containing six atoms. It may be mentioned, moreover, that cryoscopic measurements (92) indicate the presence of six or eight atoms in the molecules of sulphur when it is in solution, and that recent measurements of its density at low pressures confirm this.

179. Extracting sulphur from its ores. The purest sulphur is that collected near volcanoes. Native sulphur is usually associated with gypsum and calcium carbonate, and is supposed to have been produced either by the interacting of sulphur dioxide with hydrogen sulphide :—



or by the action of sulphuretted hydrogen, steam, and air upon chalk.

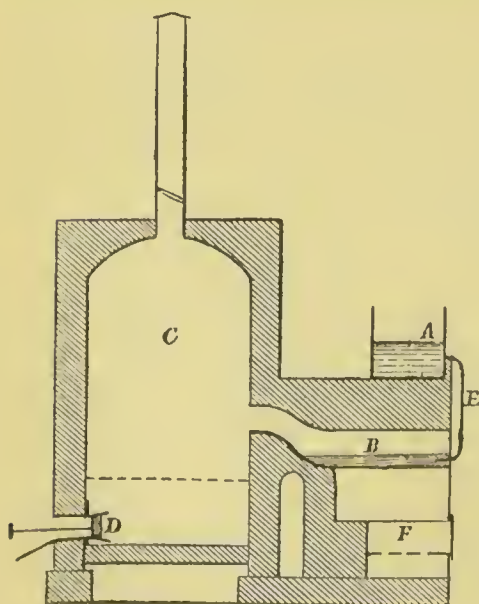


Fig. 74.

Sulphur is also obtained from pyrites. Heaps of pyrites containing as much as 2000 tons are piled upon brushwood, the latter is fired and heats the pyrites, liberating sulphur. Much of the sulphur is burnt and wasted, but about 1 per cent. of crude sulphur is afterwards collected from cavities in the heaps. The sulphur obtained from pyrites usually contains arsenic. A certain amount of sulphur is recovered from crude coal gas (303), and some from 'alkali waste' (357).

180. Refining crude sulphur. Native sulphur may be separated from stones, sand, &c.,

by melting it in pots; the impurities sink, and the molten sulphur is

decanted. It is usually refined by distilling it. In this process the sulphur is melted in a pot *A* (Fig. 74); whence it flows by *E* to a retort, *B*, in which it is boiled, the heat being supplied from *F*. Its vapour condenses in the chamber *C*. If the sulphur is distilled slowly, it condenses in a fine dust as *flowers of sulphur*; but if the sulphur enters the chamber rapidly, the latter becomes hot and then liquid sulphur collects. This is run off by *D* into moulds in which it solidifies, forming *roll sulphur*.

181. The allotropic forms of sulphur. 1. *Native or octahedral sulphur*. If you examine a good specimen of native sulphur you will find that it consists of crystals, or fragments of crystals, more

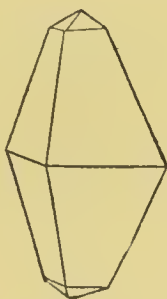


Fig. 75 a.

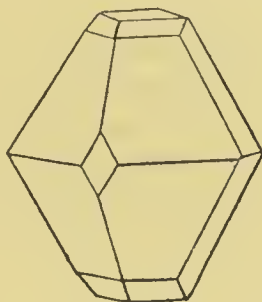


Fig. 75 b.

or less similar to the octahedra shown in Fig. 75 *a* and *b*. Similar crystals have been obtained by heating sulphur to 120° , and then cooling it in vessels surrounded by water or oil kept at 90° . They are also deposited from solutions of sulphur in carbon disulphide.

2. *Prismatic sulphur*. Melt some sulphur in a crucible, and allow it to cool in the air. When a crust has formed on its surface, pierce two holes through opposite sides of the crust, and pour off the remaining molten sulphur; now remove the crust, and you will find that the crucible contains long, amber-coloured, prismatic needles. These prismatic crystals melt at about 120° ; their density is 1.98, whilst that of octahedral sulphur is 2.05. On standing, or if they be scratched, the needles become opaque, and readily crumble, falling into small octahedra which melt a little below 115° . Sulphur is, therefore, 'dimorphous' (338).

3. *Plastic sulphur and colloidal sulphur*. If you pour some sulphur, heated to near its boiling-point, into a basin of cold water, it will form a plastic, tenacious mass. The density of plastic sulphur is

1.95. It gradually reverts, like prismatic sulphur, to the octahedral form, and hence has sometimes been used for taking casts of medals and similar objects.

A non-crystalline and soluble form of sulphur, sometimes called γ -sulphur, has been met with among the products of the interaction of sulphur dioxide, hydrogen sulphide, and water; and a somewhat similar substance may be prepared by adding strong hydrochloric acid to a strong solution of sodium thiosulphate.

4. *Amorphous sulphur.* Add some hydrochloric acid to some solution of sodium thiosulphate, collect, wash, and dry the precipitate. Examine it with a lens, and place some in carbon disulphide. You will find that it is not crystalline, and that it is partly insoluble.

Sulphur is chiefly met with in commerce as flowers of sulphur, roll sulphur, and *milk of sulphur*. The latter is made by boiling a mixture of flowers of sulphur and slaked lime with water, when a solution containing calcium polysulphide and calcium thiosulphate (CaS_2O_3) is formed; adding excess of hydrochloric acid to the solution, and washing and drying the sulphur which separates. If you digest some milk of sulphur in carbon disulphide, you will find it to be partly soluble and partly insoluble.

182. EXPERIMENT 140. Some chemical properties of sulphur.

1. Heat some sulphur in *A* till it boils gently, and pass hydrogen into it through *C*. The smell of hydrogen sulphide (H_2S) will be recognizable in the gas which escapes at *B*, and the escaping gas will blacken paper soaked in a solution of lead nitrate.

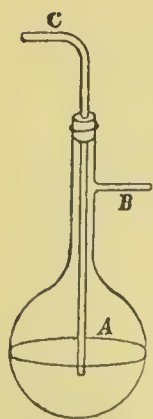


Fig. 76.

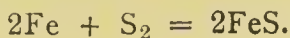
2. Heat some sulphur in an iron spoon. It will melt, and then burn, giving the well-known odour of sulphur dioxide (SO_2), which is commonly called the smell of burning sulphur.

3. Boil some sulphur in a flask or large test tube, and plunge a roll of copper foil into its vapour. The copper will become incandescent, and be converted into a brittle, black solid. This is copper sulphide.

4. Place a fragment of sodium in sulphur vapour. They will combine.

5. Heat a roll of iron wire gauze to bright redness, and press it, whilst hot, against a roll of sulphur held above a basin of water. The iron will disappear, forming a fusible substance, which congeals to metal-like globules as it falls into the water. Place one of these in

some dilute sulphuric acid. It will not evolve hydrogen, but hydrogen sulphide, for iron sulphide (FeS) has been formed :—



COMPOUNDS OF SULPHUR AND HYDROGEN.

183. Hydrogen monosulphide or sulphuretted hydrogen (H_2S). This occurs among the gases which escape from volcanoes, and in some mineral waters ; it is often found among the products of putrefaction.

EXPERIMENT 141. The preparation and physical properties of sulphuretted hydrogen. Hydrogen sulphide is usually prepared in a ' Kipp's Apparatus ' (Fig. 77). Iron sulphide is placed in *C* through *F*, and acid introduced at *A*. When the gas is wanted, *T* is opened ; the acid then passes by *E* to *C*, and acts upon the iron sulphide, generating hydrogen sulphide, which escapes through *T*. On closing *T*, the gas forces the acid back into *B* and *A*, and no more gas is generated.

Iron sulphide is apt to contain metallic iron. Hence the hydrogen sulphide produced from it may be contaminated with hydrogen. When pure hydrogen sulphide is required, antimony sulphide (Sb_2S_3) may be boiled with strong hydrochloric acid :—

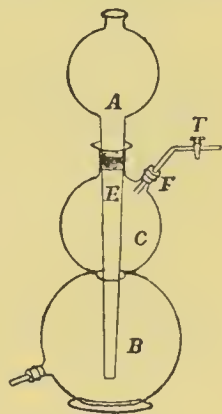
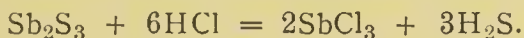


Fig. 77.

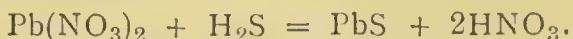
Hydrogen sulphide may also be made by heating melted paraffin wax with sulphur.

You will find that hydrogen sulphide is a colourless gas, which is not very soluble, and possesses a very characteristic, unpleasant odour. It has been condensed to a liquid lighter than water, which boils at -62° and freezes at about -85° . It is very poisonous.

EXPERIMENT 142. Some chemical properties of hydrogen sulphide. 1. Hold a sheet of silver near a jet of hydrogen sulphide. The silver will be blackened, sulphide of silver (Ag_2S) being formed.

2. Pass a few bubbles of the gas through some solution of lead nitrate ($\text{Pb}(\text{NO}_3)_2$). A black precipitate of lead sulphide (PbS) will be formed. Remove the precipitate, and add the filtrate to some blue

litmus. You will find it contains a free acid. This is formed according to the following equation :—



Make similar experiments with solutions containing salts of copper, mercury, arsenic, antimony, and cadmium.

You will obtain characteristic precipitates of metallic sulphides, viz. HgS , As_2S_3 , Sb_2S_3 , and CdS , and an acid solution*.

3. Pass hydrogen sulphide into solution of soda. It will be absorbed, a hydrosulphide being formed :—



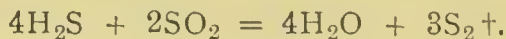
Add red litmus to the product. You will find that it is alkaline, for hydrogen sulphide cannot actually neutralize an alkali. Add some hydrogen chloride. It will give off sulphuretted hydrogen.

4. Bring a light to a cylinder filled with hydrogen sulphide. Notice that, as the gas burns, dew is formed, that solid sulphur is deposited and that some sulphur dioxide is produced. These results show us that hydrogen sulphide contains hydrogen and sulphur.

Only water and sulphur dioxide are formed by its complete combustion :—



5. Mix a cylinder of sulphur dioxide (187) with a larger cylinder containing sulphuretted hydrogen. Notice that solid sulphur is produced :—



6. Pass some chlorine or bromine into a jar containing hydrogen sulphide. Notice that sulphur is deposited and that fumes of hydrochloric acid, or of hydrobromic acid, are evolved.

7. *Is hydrogen sulphide an acid?* A solution of hydrogen sulphide is distinctly acid to litmus, and alkalis absorb it readily. Therefore we may consider it to be an acid, and may regard the metallic sulphides as the salts of this acid. It is, however, a weak acid, in the sense that though it reacts with alkalis, somewhat like hydrogen chloride, it does not neutralize them. The sulphides, moreover, are very readily decomposed by other acids.

EXPERIMENT 143. *Is sulphuretted hydrogen a reducing agent?*

* This property of hydrogen sulphide affords us a useful method of obtaining free acids, and of separating the metals from solution of their salts.

† The water may also be identified.

1. Try the tests given in 499 for ferrous and ferric salts. Then pass hydrogen sulphide through a solution of ferric chloride till the latter smells strongly of the gas. Notice that sulphur is precipitated, boil off the excess of hydrogen sulphide, and add to some of the product a drop of potassium ferrocyanide. No dark blue precipitate will form. Add to another part some potassium ferricyanide. A precipitate of Prussian blue, ferrous ferricyanide, will fall, showing that the ferric chloride (FeCl_3) has been reduced to ferrous chloride (FeCl_2):—



2. Pass sulphuretted hydrogen into some solution containing potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) acidified with sulphuric acid. Notice the change of colour which it produces. The solution no longer contains a chromate, but in its place chrome alum ($\text{K}_2\text{SO}_4, \text{Cr}_2\text{SO}_4, 24\text{H}_2\text{O}$).

3. Repeat the above experiment using potassium permanganate ($\text{K}_2\text{Mn}_2\text{O}_8$ or KMnO_4). It will be decolourized owing to the reduction of the permanganate.

4. The action of hydrogen sulphide (H_2S) on sulphur dioxide (SO_2) (Expt. 142, 5) is another example of the reducing action of hydrogen sulphide.

EXPERIMENT 144. To find the composition of hydrogen sulphide. Hydrogen sulphide can be produced by the union of hydrogen and sulphur (Expt. 140); therefore it contains these two elements only.

Place some fragments of granulated tin in *B* (Fig. 78), close *C*; fill the bend of *A* with mercury; pass hydrogen sulphide through the apparatus from *T* till all the air is displaced; fill up *A* with mercury to the level *a*, opening *T* slightly while you do so. Then close *T* and

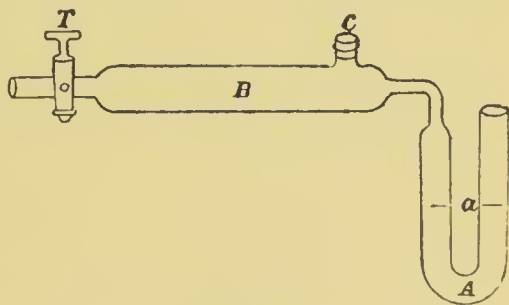


Fig. 78.

heat the tin. Some of the sulphuretted hydrogen will be destroyed, forming tin sulphide and liberating hydrogen.

Allow the apparatus to cool, and note the position of the mercury in *A*. It will be the same as at the beginning of the experiment.

Therefore the volume of the hydrogen liberated is equal to that of the hydrogen sulphide destroyed.

That is to say, hydrogen sulphide contains its own volume of hydrogen.

But unit volume of hydrogen sulphide weighs seventeen times as much as unit volume of hydrogen*.

Therefore 17 parts of hydrogen sulphide contain one part of hydrogen and, since it contains only sulphur and hydrogen, 16 parts of sulphur.

If we calculate the percentage composition of the gas from these data we find it to be—

Hydrogen	5.9
Sulphur	94.1
	100.0

184. Hydrogen persulphide or hydrogen disulphide (H_2S_2). EXPERIMENT 145. To make hydrogen disulphide. Boil a mixture of slaked lime and sulphur in equal proportions with about ten times their weight of water. Filter off the orange-coloured solution, and pour it into a mixture of equal volumes of strong hydrochloric acid and water gently warmed. The mixture will not deposit a white precipitate of milk of sulphur, but a heavy yellow oil which may be withdrawn from under the water by means of a pipette.

Heat a little of the yellow oil in a test tube. Hydrogen sulphide will be given off, and sulphur will be left, from which it seems clear that the oil is a compound of hydrogen and sulphur, and that it contains more sulphur than hydrogen monosulphide.

It is difficult to ascertain the composition of hydrogen disulphide with certainty, in consequence of its instability. When it is analysed, more sulphur is found in it than is required for the formula H_2S_2 . But this may very well be due to the presence of sulphur held in solution, for we have seen that the compound is readily resolved into hydrogen sulphide, which escapes, and sulphur, which remains with the undecomposed portion of the compound. In consequence of certain analogies between this substance and hydrogen peroxide, and of the general resemblance between many of the compounds of oxygen and sulphur, the above formula is usually adopted. The probability that it may be correct is increased by the fact that strychnia forms

* i. e. its density is 17.

a crystalline substance, which has the formula $2C_{21}H_{22}N_2O_2 \cdot 3H_2S_2$, and which yields oily drops of the disulphide when it is decomposed with sulphuric acid.

The student should carefully compare the processes by which he obtained milk of sulphur and hydrogen persulphide, and take note of the difference in procedure which determines whether we obtain the one substance or the other from the same materials.

185. The sulphides. These compounds are mostly decomposed by acids with liberation of hydrogen sulphide, and sulphides of the alkali metals are soluble and alkaline to litmus, but most of the others are insoluble. They are converted into sulphates by oxidizing agents, and many of them occur free in nature. The most important sulphides are described in the following pages.

186. The oxides and acids of sulphur. Four oxides of sulphur are known. Three of these are acid anhydrides. They are—

Sulphur dioxide (SO_2), corresponding to sulphurous acid (H_2SO_3).

Sulphur trioxide (SO_3), corresponding to sulphuric acid (H_2SO_4).

Sulphur sesquioxide (S_2O_3).

Sulphur heptoxide (S_2O_7), corresponding to persulphuric acid ($H_2S_2O_8$ or HSO_4).

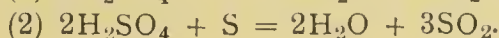
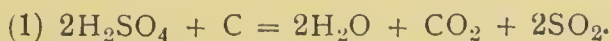
187. Sulphur dioxide or sulphurous anhydride (SO_2). We have obtained this gas by burning sulphur in oxygen. In nature it occurs among volcanic gases; and it is present in air contaminated by the products of burning coal or impure coal gas.

EXPERIMENT 146. To make sulphur dioxide. Heat scraps of copper with oil of vitriol in a flask provided with a delivery tube, and collect the gas in cylinders by downward displacement of air. The following change occurs :—



but the dark residue left in the flask contains copper sulphide.

Mercury or lead may be used in place of copper; if these be used no metallic sulphide will be formed. Charcoal or sulphur may also be employed :—



Other methods of making sulphur dioxide.

1. As sulphuric acid is itself made from sulphur dioxide, the above are merely laboratory methods. On the large scale, sulphur dioxide is chiefly made by burning sulphur or pyrites (FeS_2) (see sulphuric acid, 194).

2. Sulphur dioxide may be obtained from sodium thiosulphate (Expt. 155).

3. Dry iron sulphate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) may be heated with sulphur:—



EXPERIMENT 147. To study the properties of liquid sulphur dioxide. When making the last experiment you will have noticed that sulphur dioxide is a colourless gas and possesses the odour of burning sulphur.

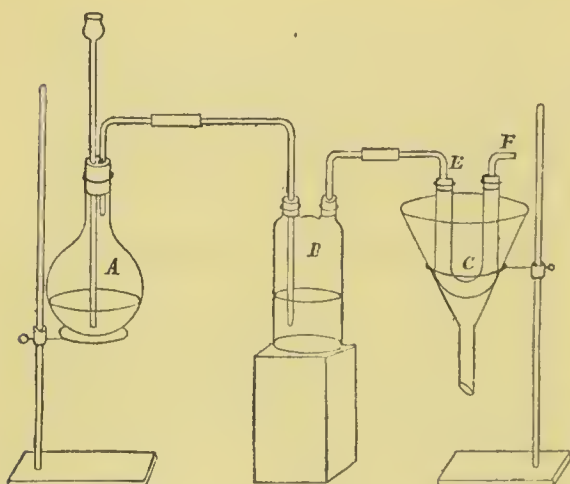


Fig. 79.

Generate sulphur dioxide from copper and sulphuric acid in *A* (Fig. 79), pass it through strong sulphuric acid in *B* to dry it, then into a U tube *E*, surrounded with a freezing mixture of ice and salt in *C*, and conduct any uncondensed gas to a flue through *F*.

The sulphur dioxide will soon collect in *E* as a colourless liquid.

If you immerse the bulb of a thermometer in the liquid sulphur dioxide it will boil violently, and the thermometer will fall to -10° ; if you can immerse a tube containing a few drops of the liquid sulphur dioxide in a mixture of solid carbonic acid and ether, it will freeze to a solid which melts at about -79° . Sulphur dioxide dissolves several of the non-metals, and mixes with such liquids as ether, benzene and chloroform.

EXPERIMENT 148. Some chemical properties of sulphur dioxide. 1. Pass some sulphur dioxide into some water; it will dissolve, 1 volume of water absorbing 30 volumes of the gas. The solution, which reddens litmus, has the odour of sulphur dioxide; if some

of it is added to an alkaline carbonate, carbon dioxide will be displaced, and the liquid will yield a salt if it be evaporated.

Therefore we may conclude that sulphur dioxide forms an acid with water. This acid (H_2SO_3) is called *sulphurous acid*.

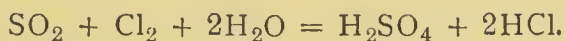
2. Sulphur dioxide, or its solution in water, is a reducing agent.

(a) Add a drop of sulphurous acid to a solution of iodic acid. Iodine will be liberated owing to the reduction of the latter (see also 164).

(b) Warm some potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) with some dilute sulphuric acid, and pass sulphur dioxide through the mixture. The bichromate will be reduced, yielding a green solution which contains chrome alum ($\text{K}_2\text{SO}_4, \text{Cr}_2\text{SO}_4, 24\text{H}_2\text{O}$).

(c) Add some sulphurous acid to a solution of permanganate of potassium, and compare its effect with that of hydrogen sulphide (Expt. 143, 3).

(d) Sulphur dioxide is sometimes used as an 'antichlor' for destroying excess of chlorine in substances which have been bleached by means of that element. The sulphur dioxide is converted into sulphuric acid, which must be removed by washing on account of its destructive nature:—



(e) Place a delicately-tinted flower, such as the bloom of an azalea, or a primrose, in a jar of sulphur dioxide. It will lose its colour.

Sulphur dioxide is extensively used to bleach substances which would be injured by chlorine, such as woollen cloth, silk, leather, straw, and sponge. It is thought that its action may depend upon its activity as a reducing agent (compare chlorine, 137); but in some cases colourless substances are probably produced by the combining of the dioxide with the colouring-matter.

Sulphur dioxide also destroys the organisms which are associated with putrefaction. It may therefore be employed as a disinfectant; wine casks are cleansed by burning sulphur within them, and rooms are fumigated with burning sulphur.

188. The composition of sulphur dioxide. EXPERIMENT 149. A method of finding the composition of sulphur dioxide. Place a splinter of sulphur in the coil of platinum wire *C*, over a boat *S* (Fig. 80). Fill *A* with oxygen, by displacing the air, and fix the

stopper firmly in position. Note the level of the mercury a a' and heat the coil of platinum by passing a current of electricity through it. The sulphur will then burn, forming sulphur dioxide. When the combustion is complete, and the apparatus has cooled to its original temperature, the volume of the gas in A will be found to be nearly unaltered. Therefore every volume of oxygen consumed by the sulphur has been replaced by an equal volume of sulphur dioxide.

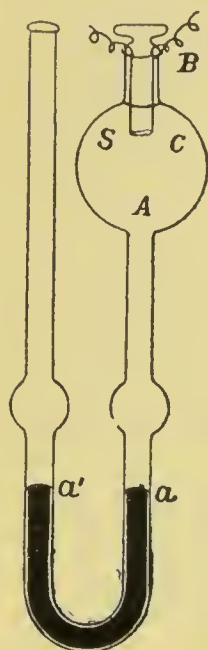


Fig. 80.

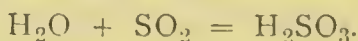
That is to say, 1 volume of sulphur dioxide contains 1 volume of oxygen.

If we substitute for the equal volumes of the two gases the weights of equal volumes (i.e. their densities), viz. 32 and 16*, we find that 32 parts of sulphur dioxide contain 16 parts of oxygen and 16 parts of sulphur, so that the percentage composition of the gas is:—

Sulphur	50 parts
Oxygen	50 „
	100

In practice, the observed volumes of the oxygen and sulphur dioxide probably would not be exactly equal. If the student does not remember how Gay-Lussac's law of volumes applies to such a case he should refer to 83.

189. Sulphurous acid. The acid formed by dissolving sulphur dioxide in water is known by this name (see Expt. 148, 1). It is very instable and has not been obtained in the pure state. From its mode of formation, its formula may be supposed to be H_2SO_3 :—



Sulphurous acid should yield two classes of salts, viz. hydric sulphites, such as NaHSO_3 , and normal sulphites, such as Na_2SO_3 ; both are known.

190. The sulphites. Many of the metals form sulphites. As a rule these salts may be recognized by the following tests.

1. Add dilute sulphuric acid to sodium sulphite, and warm the mixture. Sulphur dioxide will be given off, and may be recognized by its odour.

* Of course these must be known, or determined for the purpose.

2. Expose a dilute solution of an alkaline sulphite to the air for a few days. Then add some solution of barium chloride. A white precipitate of barium sulphate, which is insoluble in dilute nitric acid, will fall.

Repeat the last part of the experiment, using some freshly made solution of sodium sulphite. The precipitate produced, which is barium sulphite, will dissolve in dilute nitric acid.

Nascent hydrogen (see 137) reduces sulphites to sulphides. Therefore, if zinc and dilute sulphuric acid be added to a sulphite in solution, hydrogen sulphide will be liberated.

The sulphites of the metals of the alkalis are soluble, and may be divided into hydric sulphites and normal sulphites (see above). They are easily made by passing sulphur dioxide into solutions containing the hydroxides or carbonates of the metals. Insoluble sulphites may be prepared from solutions of soluble salts by precipitation.

191. Sulphuric anhydride or sulphur trioxide (SO_3).

EXPERIMENT 150. To prepare and study the properties of sulphur trioxide. 1. Pass sulphur dioxide and oxygen through

the tubes 1, 2 (Fig. 81), into a wash-bottle containing strong sulphuric acid *C*, and thence over strongly heated platinized asbestos* in *A*. Dense fumes will escape at *B*: these consist of sulphur trioxide (SO_3). They may be condensed in a well-cooled tube, or led into water, in which they will dissolve forming sulphuric acid:—

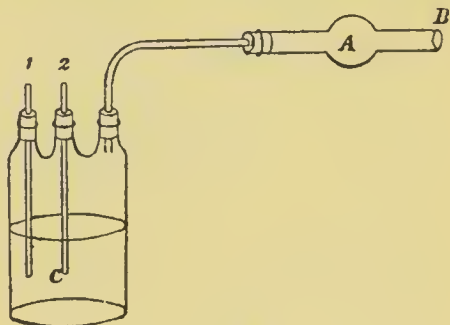
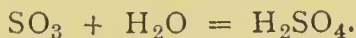
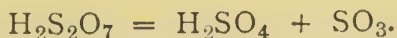


Fig. 81.



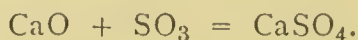
2. If some Nordhausen sulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$) (193) be distilled in a retort, similar white fumes of sulphur trioxide will be given off. They are formed according to the following equation:—



Sulphur trioxide must be preserved in tubes sealed hermetically.

* To prepare this soak asbestos in solution of platinic chloride, drain and ignite.

It forms beautiful silky needles, melts at about 15° , and boils at about 46° . When dry it has no action on litmus, but it absorbs moisture from the air with great avidity, forming sulphuric acid. If it be passed over a basic oxide, such as lime (CaO), kept hot, the two oxides will combine vigorously:—



This reaction affords us an example of the formation of a salt by the direct union of a basic oxide with an acidic oxide.

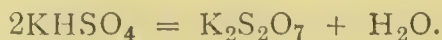
If sulphur trioxide be passed through a red-hot tube, sulphur dioxide and oxygen are formed from it.

192. Oil of vitriol or sulphuric acid (H_2SO_4). We have just learnt that this important acid may be formed by dissolving sulphur trioxide in water, and that some of its salts are produced by the atmospheric oxidation of sulphites in solution.

Sulphuric acid was formerly made from green vitriol ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and its older name, 'oil of vitriol,' is derived from this mode of making the acid.

193. Fuming sulphuric acid. If ferrous sulphate be heated in air and then distilled, it gives off fumes containing sulphuric acid and sulphur trioxide, and leaves ferric oxide (Fe_2O_3) in a state of fine division*. The sulphuric acid and the trioxide of sulphur condense to form an oily fuming liquid known as *Nordhausen* or fuming sulphuric acid, which may be supposed to contain *anhydrosulphuric acid* ($\text{H}_2\text{SO}_4 \cdot \text{SO}_3$, or $\text{H}_2\text{S}_2\text{O}_7$). Fuming sulphuric acid is used for dissolving indigo, in the manufacture of the dye alizarine, and in gas analysis.

The sodium and potassium salts of this acid, the pyrosulphates, or anhydrosulphates, of potassium and sodium, may be made by heating the corresponding acid sulphates to low redness, hence the name pyrosulphate:—



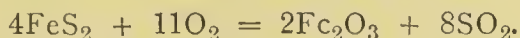
When heated with strong sulphuric acid, these salts evolve sulphur trioxide.

194. The manufacture and properties of sulphuric acid. Sulphuric acid is made in enormous quantities from sulphur dioxide, by taking advantage of the fact that the latter substance is converted

* This residue is the 'rouge' of the jeweller, and is useful as a pigment

into sulphuric acid, when it is exposed to the action of nitric peroxide (N_2O_4) (237), in the presence of water-vapour.

When the acid is required free from arsenic, the sulphur dioxide is prepared by burning sulphur, but most of our sulphuric acid is made from iron pyrites (FeS_2)*. This is burnt in a series of furnaces, marked *A* on the conventional ground plan given in Fig. 82, and yields sulphur dioxide and ferric oxide (Fe_2O_3):—



The sulphur dioxide, together with excess of air, passes from the burners through a flue,

or chamber, in which pots containing nitre and sulphuric acid are placed to supply nitric acid †; thence they go through *B* into a series of chambers, *C*, *C'*, *C''*, constructed of lead, where they meet the necessary water, which is supplied, as steam, through numerous jets.

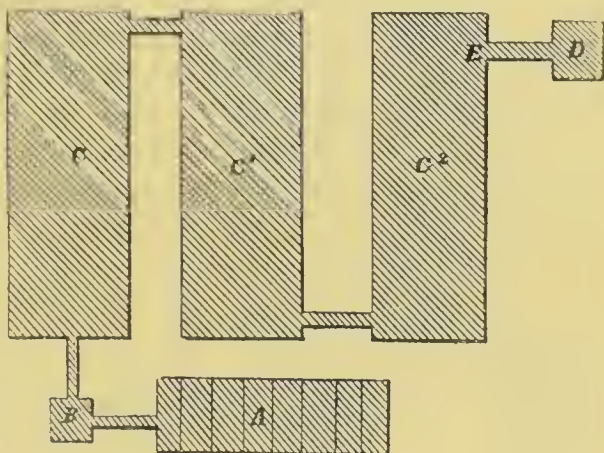


Fig. 82.

These vitriol chambers, as they are called,

vary a good deal in size, about 33 metres long, by 8 wide, and 5 metres high being a not unusual size. As the gases pass through the chambers, sulphuric acid forms, and condensing, falls to the floor in the form of 'chamber acid,' which may contain about 65 per cent. of real sulphuric acid (H_2SO_4).

The theory of the changes which take place in a vitriol chamber is still under discussion, but the following equations will give a fair idea of the nature of the process, even if they do not represent the reactions quite correctly:—

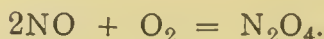
1. Sulphur dioxide, nitric acid, and steam react, producing sulphuric acid and nitric oxide:—



* The best pyrites comes from Spain. This is rich in sulphur, and also contains copper, which can be profitably extracted from the burnt ore.

† $2\text{KNO}_3 + \text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{HNO}_3.$

2. The nitric oxide (NO) is reoxidized by the air to nitric peroxide (N_2O_4) (see 237):—



3. The peroxide thus formed oxidizes more sulphur dioxide in the presence of steam:—



The nitric oxide is then again converted into peroxide by more air, oxidizes yet more sulphur dioxide, and so on, so that a comparatively small quantity of nitric oxide carries oxygen to a relatively large amount of sulphur dioxide*.

The nitric oxide cannot, however, oxidize an unlimited amount of sulphur dioxide. This is partly because the contents of the chamber gradually become too much diluted with nitrogen, partly because by the time the gases reach *E*, all the available sulphur dioxide is consumed, and partly because some nitric oxide is lost in secondary reactions, in which it is reduced to nitrous oxide (N_2O). Consequently, the nitric acid from 3.5 to 4 kilograms of nitre must

be added for every 33 kilograms of sulphur converted into dioxide, unless some method, such as that presently described, be employed to reduce the consumption of nitre.

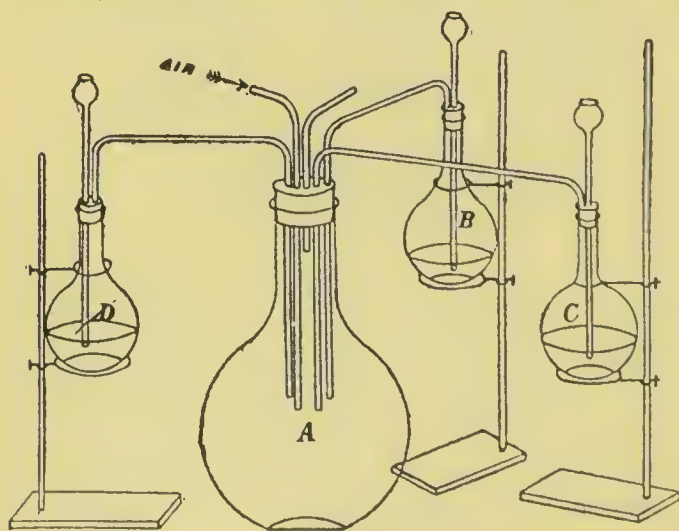
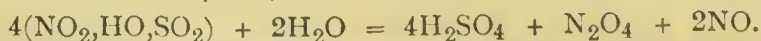


Fig. 83.

scale. Pass slowly into a very large flask *A* (Fig. 83) sulphur dioxide from *D* (Expt. 146); nitric oxide from copper and diluted nitric acid

* According to another hypothesis a white crystalline substance, nitro-sulphonic acid ($\text{NO}_2 \text{ } \left\{ \begin{smallmatrix} \text{NO}_2 \\ \text{HO} \end{smallmatrix} \right\} \text{SO}_2$), is formed and then decomposed by steam:—



The oxides of nitrogen and oxygen are then supposed to form more nitro-sulphonic acid, which again reacts with water.

EXPERIMENT
151. To make chamber crystals and sulphuric acid on the small

in *C* (239); air from a bellows, and a little steam from *B*, if the nitric oxide be not sufficiently moist. The sides of the flask will soon be coated with chamber crystals. When these appear, supply the steam more liberally. The crystals will quickly disappear, yielding a liquid which will give the reactions of sulphuric acid.

Concentrating the sulphuric acid produced in the chambers. Chamber acid contains about 65 per cent. of real sulphuric acid. It is concentrated, first, by evaporating the weak acid in glass or leaden basins till acid fumes begin to come off; and finally by distilling the partly concentrated acid from retorts of glass or platinum (Fig. 84). At the latter stage, weak sulphuric acid is at first given off, then a stronger acid, and so on, till at length the density of the residue is about 1.84, at 0°. The strongest acid thus produced contains about 98 per cent. of true acid; it cannot be further concentrated by distillation.

Arsenic and nitrous compounds may be removed from sulphuric acid by distilling it with ammonium chloride. The arsenic passes off, as chloride, in the first portions of the distillate, whilst the nitrous compounds and the ammonia produce nitrogen and water.

Gay-Lussac tower. To avoid waste of nitre, the spent gases, which still contain nitric oxide when they escape from the chambers at *E*, are exposed to strong sulphuric acid in the Gay-Lussac tower *D* (Fig. 82). The nitrous fumes are absorbed, and the solution is pumped to the top of a Glover tower *B*. In *B* the nitrated acid and chamber acid are allowed to flow over flints. Nitrous fumes are liberated from the former, by the gases from *A*, and escape, leaving behind sulphuric acid. The mixture of hot sulphur dioxide, nitric acid, and air from the pyrites burners ascends this tower, and sweeps the oxide of nitrogen into the chambers. The sulphuric acid runs to the bottom of the tower, and is reconcentrated by the hot gases which pass over it as it descends.

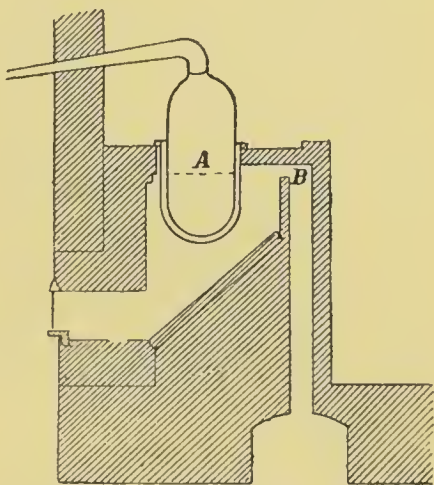


Fig. 84. The retort *A* is heated by hot gases, from a fire, which reach the retort by the flue *B*; *A* is so placed that upper layers of the acid are most strongly heated.

195. Real Sulphuric acid H_2SO_4 . To prepare this, sulphuric anhydride must be added gradually, and in proper proportion, to oil of vitriol which has previously been cooled.

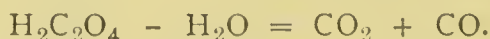
196. Some properties of sulphuric acid. As usually met with, sulphuric acid is an oily liquid nearly twice as dense as water. It is very hygroscopic and decomposes the salts of many other acids, as may be learnt from the following experiment :—

EXPERIMENT 152. 1. Expose a weighed beaker containing sulphuric acid to the air for a few hours, then reweigh it. You will find its weight has increased. This is due to the oil of vitriol having absorbed water from the air.

2. Mix 50 c.c. of strong sulphuric acid *gradually* with 40 c.c. of water. The temperature of the mixture will rise considerably above 100° , and if a small test tube containing water be immersed in it, the water will boil vigorously.

Several definite hydrates of sulphuric acid are known; one of these has the formula $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. It may be obtained by diluting some oil of vitriol till its density is 1.78, and cooling the mixture, when it will solidify at about 7° . A second hydrate corresponds to the formula $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$.

3. Warm some oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) with strong sulphuric acid. A colourless combustible gas will be evolved. This contains carbon monoxide (CO). Pass some of the gas through lime-water. You will find that carbon dioxide is also present. These gases are formed in consequence of the sulphuric acid abstracting water from the oxalic acid :—



4. Paint some letters on a sheet of paper with sulphuric acid, and warm the paper before a fire or in an air bath. It will be carbonized.

5. Mix a little strong warm syrup with some strong sulphuric acid in a capacious beaker. The sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) will lose the elements of water, and will be reduced to a carbonaceous mass.

How do you account for this mass having the odour of sulphurous acid?

The dehydrating power of sulphuric acid is often made use of by chemists. Thus we employ this acid to dry many gases, and we make carbon monoxide from oxalic acid, and ethylene (C_2H_4) from alcohol ($\text{C}_2\text{H}_6\text{O}$), by warming them with oil of vitriol.

6. Place scraps of zinc or iron in strong sulphuric acid. Notice that little or no effect is produced. Then apply heat, and notice that the acid is reduced, sulphur dioxide, and possibly hydrogen sulphide or free sulphur, being formed. On the other hand we have seen that zinc and iron yield hydrogen with dilute sulphuric acid *. This difference between the action of strong and weak sulphuric acid on certain metals should be carefully remembered.

7. Place a *small* fragment of sodium in some strong sulphuric acid. Hydrogen will be evolved (this experiment should be done by the teacher). Thallium behaves similarly, but only a few metals thus set free hydrogen from strong sulphuric acid.

8. Dilute some commercial oil of vitriol. A white precipitate will probably fall. This consists of lead sulphate previously dissolved from the 'vitriol chambers' or concentrating pans by the acid. If the precipitate be collected, and reduced on a block of carbon with a little potassium cyanide, it will yield a bead of lead.

9. Connect a galvanic battery with some strong sulphuric acid. You will find that the acid is but slowly decomposed.

Repeat the experiment, using diluted sulphuric acid. The current will now pass through the acid freely, and the water will be decomposed much more rapidly.

We have already seen that sulphuric acid displaces many acids from their salts (e.g. Expt. 115), and that sulphuric acid and the sulphates give white precipitates of barium sulphate (BaSO_4) with solutions containing salts of that metal.

Shake up some air in a bottle with strong sulphuric acid. Then hold a slip of bibulous paper, previously dipped in a solution containing iodide of potassium and starch, in the air. If the paper turns blue, nitrous compounds are present in the acid.

197. The molecular weight of sulphuric acid. The apparent vapour density of sulphuric acid is about 25, which would lead us to conclude that the molecular weight of the acid must be about 50 (91).

But the study of the compounds of sulphur, other than sulphuric acid, has led chemists to conclude that the atomic weight of sulphur is 32.

Now as atoms are indivisible a molecular proportion of sulphuric acid cannot contain less than one atomic proportion of sulphur. That is, not less than 32 parts of sulphur.

* Ascertain whether copper behaves similarly in dilute acid.

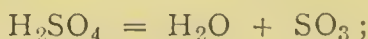
But 32 parts of sulphur are contained in 98 parts of sulphuric acid.

Hence the molecular weight of sulphuric acid must be 98 or some multiple of 98.

Again, it is possible to replace the hydrogen of sulphuric acid by sodium, or potassium, in two stages (see 114). At the first stage, 23 parts of sodium* replace half the hydrogen in 98 parts of the acid, producing a definite salt which contains sodium and hydrogen in atomic proportions. At the second stage, 23 parts of sodium replace the remaining hydrogen and produce a second and distinct salt which contains no hydrogen. These facts are held to imply the presence of at least 2 atoms of hydrogen in every molecule of sulphuric acid. But 2 parts of hydrogen are contained in 98 parts of sulphuric acid, and therefore 98 is the smallest value we can adopt for the molecular weight of this acid.

198. The effect of heat on sulphuric acid. Dissociation †.

The fact that the vapour density of sulphuric acid is abnormal threw considerable doubts on the validity of Avogadro's hypothesis (91), until it was suggested that the acid might possibly split into water and sulphur trioxide when volatilized. Thus:—



in which case one molecular proportion of the acid would not produce *two* volumes of the vapour of sulphuric acid, but *four* volumes of a mixture of water-vapour and sulphur trioxide, the mean density of which would be just half as great as that of the undecomposed sulphuric acid. It was further pointed out that such a change might very well be overlooked if the water and sulphur trioxide should recombine on cooling, as might be expected.

This hypothesis was tested in the following manner. We have seen that gases diffuse at rates which are inversely proportional to the square roots of their densities (129). From this it follows that if a mixture of steam (H_2O , $D = 9$) and sulphur trioxide ($D = 40$) were permitted to diffuse from a flask, the steam would escape much more quickly than the sulphur trioxide. Accordingly, some sulphuric acid of known composition was heated for some time to a temperature above its boiling-point in a flask provided with a capillary neck, and afterwards

* i. e. one atomic proportion.

† See also phosphoric chloride (254), and ammonium chloride (220).

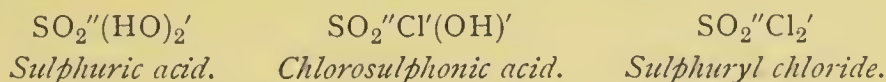
reanalysed. The residual acid was found, as had been expected, to contain a greater proportion of sulphur trioxide than that taken for the experiment. Changes of this class are termed reversible; they are often written as follows:—



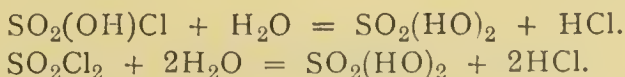
199. The basicity and constitution of sulphuric acid.

Sulphuric acid yields two classes of salts with univalent metals, such as lithium, sodium and potassium; thus for example with sodium we can get a hydric salt NaHSO_4 , and a normal salt Na_2SO_4 (114); or, to express the matter differently, we believe that a molecular proportion of sulphuric acid requires two equivalent proportions of a base to neutralize it. It is therefore said to be *dibasic*.

If strong sulphuric acid (H_2SO_4) is treated with chloride of phosphorus (253), it exchanges an atom of hydrogen and one of oxygen for an atom of chlorine, producing the compound ClHSO_3 (chlorosulphonic acid), which would seem to be formed through the replacing of one hydroxyl group (HO) by an atom of chlorine in each molecule of sulphuric acid. If this compound is heated to 158° , part of it yields sulphuryl chloride (SO_2Cl_2), which may be regarded as sulphuric acid ($\text{SO}_2(\text{HO})_2$) in which the two hydroxyl groups are replaced by two atoms of chlorine. These relations among the three substances are expressed by the following formulæ:—

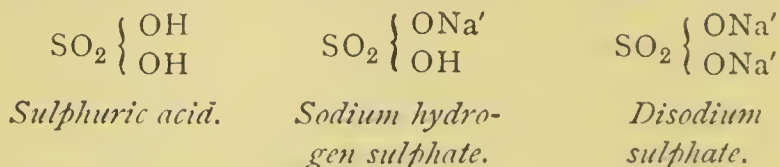


in which sulphuric acid is represented as being the hydroxide of sulphuryl (SO_2), or as having a constitution analogous to that of calcium hydroxide ($\text{Ca}(\text{HO})'_2$) except that a compound radicle replaces the atom of calcium. The ideas concerning the constitution of the molecule of sulphuric acid, drawn from these compounds, are confirmed by the existence of other analogous compounds, and by the fact that chlorosulphonic acid ($\text{SO}_2\text{Cl}(\text{OH})$) and sulphuryl chloride (SO_2Cl_2) when acted on by water again exchange chlorine for hydroxyl. Thus:—



As the sulphates are formed by replacing the hydrogen of sulphuric

acid by metals, their constitutional formulæ take such forms as those which follow * :—



200. Constitution of the oxyacids. Sulphuric acid is not the only acid which is capable of exchanging hydroxyl for chlorine, when acted on by such compounds as the chlorides of phosphorus or phosphoryl chloride. Other acids, and other compounds containing hydroxyl, behave in a similar manner. The circumstance that the number of hydroxyl groups in an acid frequently corresponds to the basicity of the acid, leads us to conclude that the basic hydrogen of the oxyacids is likely to be hydroxylic.

201. Salts of sulphuric acid. Sulphates. The general methods of making salts mentioned in 115 may be applied to the salts of sulphuric acid. With the exception of the sulphates of calcium, barium, strontium and lead, the sulphates are mostly soluble in water, and very many of them crystallize with water of crystallization. In some cases this water can be completely driven off by heating the salt to about 100°; for example, crystals of sodium sulphate can be dried at this temperature, but if copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) be thus moderately heated, it yields a salt corresponding to the formula $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, from which the last molecule of water can only be expelled at a higher temperature. This last portion of water is called *water of constitution* or *water of halhydration*, and the formula of the compound is occasionally written CuH_2SO_5 , with the idea that the salt may correspond not to ordinary sulphuric acid (H_2SO_4), but to another hydrate (H_4SO_5).

The following are examples of salts of this class :—

Magnesium sulphate		$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Zinc sulphate		$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Iron sulphate		$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Nickel sulphate		$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

* Constitutional formulæ, such as those given above, must not be supposed to represent the actual arrangements of the atoms in space. Their purpose is not so much to tell us how the atoms are arranged, as to enable us to foresee the probable reactions of the substances they represent.

Such salts frequently form compounds in which a molecule of water is replaced by a molecule of an alkaline sulphate. Thus nickel sulphate forms $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

The following are among the most important of the sulphates :—

Sulphate of sodium or salt-cake	see 357
Sulphate of iron or green vitriol	„ 499
Sulphate of aluminium	„ 431
Sulphate of copper or blue vitriol	„ 539
Sulphate of ammonium	„ 374
Sulphate of magnesium or Epsom salts . . .	„ 404
Sulphate of calcium or gypsum, alabaster, or plaster of Paris	„ 385
Sulphate of barium, or heavy spar, or barytes .	„ 397
Sulphate of strontium or cœlestine	„ 392

The alums. These form an interesting class of double sulphates of the type $\text{M}_2'\text{SO}_4 \cdot \text{M}''_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$. Common alum (K_2SO_4 , $\text{Al}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$) and chrome alum (K_2SO_4 , $\text{Cr}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$) (see 482) are good examples of alums.

In the general formula M' stands for potassium, ammonium, and certain other univalent metals, such as silver, thallium, cæsium, and rubidium; whilst M'' stands for aluminium, chromium, iron, and a few other metals, such as manganese, and gallium, which also form alums.

The alums are all soluble, but one or two of them are decomposed by hot water, and some of them are coloured; they afford us some excellent examples of *isomorphism* (338). Their crystals are usually regular octahedra or cubes (see 339), and it is easy to produce them of considerable size.

EXPERIMENT 153. Some properties of the sulphates. 1. Add a little barium chloride, dissolved in water, to some solution of a soluble sulphate. A precipitate of barium sulphate (BaSO_4) will fall. This compound will be found to be insoluble in *dilute* hydrochloric acid.

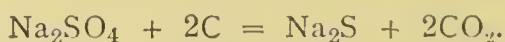
2. Add some solution of lead nitrate to a solution of a sulphate. Lead sulphate (PbSO_4) will be thrown down.

3. Heat a little solid sodium sulphate, previously dried, strongly. No signs of decomposition will be observed.

4. Heat a crystal of sulphate of iron or copper strongly. Acid fumes, containing sulphur dioxide (SO_2) and oxygen, will be given off,

and oxide of the metal will remain, for the sulphates of the heavy metals are decomposed by heat.

5. Heat some sodium sulphate mixed with carbon in the reducing flame of a blow-pipe strongly, and add a drop of dilute acid to the residuc when it is cool. Hydrogen sulphide will be evolved, for alkaline sulphates are reduced by carbon at high temperatures:—



Repeat the experiment using copper sulphate. No such result will be obtained.

Repeat the experiment using copper sulphate with a little sodium carbonate. A sulphide will again be formed.

202. Sulphur sesquioxide (S_2O_3). If sulphur trioxide be heated with sulphur a bluish-green instable crystalline solid (S_2O_3) is obtained.

203. Hyposulphurous acid ($\text{H}_2\text{S}_2\text{O}_4$). EXPERIMENT 154. Add some sulphurous acid to solution of indigo. The indigo will not be bleached.

Add scraps of zinc to some sulphurous acid, and when the solution has become yellow add a drop of the product to a little solution of indigo. The indigo will now be quickly bleached owing to the presence of a salt of hyposulphurous acid in the liquid. Hyposulphurous acid has not been isolated, but a solution of it has been made, and its sodium salt ($\text{Na}_2\text{S}_2\text{O}_4$) has been prepared. Moist sodium hyposulphite is oxidized rapidly by the air. Its solution bleaches strongly, and is a powerful reducing agent.

A solution of indigo just decolourized by means of a hyposulphite forms a very delicate test for oxygen, as a mere trace of that element will restore the colour of the indigo.

204. Sulphur heptoxide (S_2O_7). **Persulphuric acid** ($\text{H}_2\text{S}_2\text{O}_8$). Sulphur heptoxide is formed when a mixture of sulphur dioxide and oxygen is submitted to the action of the silent discharge of electricity. It is a viscid liquid, which is very volatile, and solidifies at 0° ; it forms sulphuric acid and oxygen when dissolved in water.

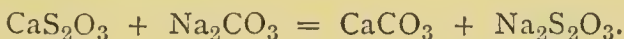
Persulphuric acid is chiefly known through its salts. To make the potassium salt a porous pot containing dilute sulphuric acid is placed in a platinum dish containing a saturated solution of potassium

hydrogen sulphate. The positive electrode of a battery is then placed in the potassium hydrogen sulphate, and the negative electrode in the acid, and a current of 3 ampères is passed through the system. After some delay crystals of potassium persulphate (KSO_4 or $\text{K}_2\text{S}_2\text{O}_8$) are deposited. Potassium persulphate is a strong oxidizer, liberating iodine from iodides and oxidizing ferrous salts. If it is heated it yields a sulphate, oxygen, and sulphuric anhydride :—



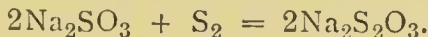
205. Thiosulphuric acid ($\text{H}_2\text{S}_2\text{O}_3$). This acid is known to us best through its sodium salt ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), which is largely used by photographers under the name of *sodium hyposulphite* or 'hypo.'

Sodium thiosulphate is made from 'alkali waste,' and from the lime used to remove sulphur compounds from crude coal gas (303). This is exposed to the air, and becomes charged with calcium thiosulphate (CaS_2O_3), which is extracted with water, and decomposed by means of sodium carbonate :—

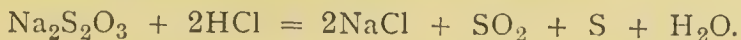


The soluble sodium thiosulphate is obtained in crystals by concentrating the filtered solution.

EXPERIMENT 155. I. To prepare a solution containing sodium thiosulphate. Heat together in a flask flowers of sulphur, sodium sulphite and water. Filter the product, and add a little acid to it. You will obtain a precipitate of amorphous sulphur, whilst sulphur dioxide will escape, showing that a thiosulphate has been formed :—



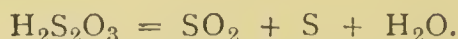
II. The properties and uses of sodium thiosulphate. 1. Add a little hydrochloric acid to a solution of the salt. Sulphur dioxide will be liberated, and sulphur will be precipitated :—



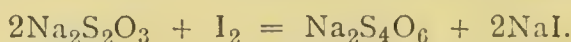
2. Add dilute acid and zinc to a solution of sodium thiosulphate. Hydrogen sulphide will be evolved, and sulphur precipitated.

3. Prepare a little silver chloride, or bromide, by adding a suitable metallic halide to solution of silver nitrate. Then pour some solution of 'hypo' on the freshly precipitated halide. The latter will at once dissolve. For an application of this, see 554.

Thiosulphuric acid has not been obtained in the free state, except in extremely dilute solutions, as it decomposes at once when liberated from its salts. Thus:—



4. Add some solution of iodine to a solution of sodium thiosulphate. The iodine will disappear; the following reaction taking place:—



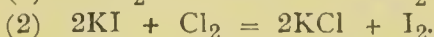
The salt $\text{Na}_2\text{S}_4\text{O}_6$ is sodium tetrathionate (206). Sodium thiosulphate is often used in volumetric analysis, for determining the strength of solutions containing free iodine or free chlorine. It is also useful as an 'antichlor' (Expt. 148, 2, d), and may be used for preparing sulphur dioxide.

Exercise for the student. To find the available chlorine in bleaching powder. Prepare a solution containing 24.8 grams of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in each litre.

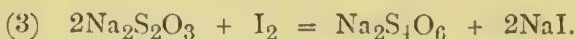
Then each cubic centimetre of this solution will contain $\frac{158}{10000}$, or 0.0158 gram, of the salt $\text{Na}_2\text{S}_2\text{O}_3$.

Weigh out a little bleaching powder, add it to some water containing excess of iodide of potassium. Then add sufficient hydrogen chloride to the mixture to dissolve the bleaching powder.

Chlorine will be set free, and will liberate an equivalent amount of iodine, according to the following equations:—



Dilute the product to a convenient known volume, and titrate measured portions of the solution of iodine thus prepared with the solution of sodium thiosulphate:—



From the given equations we see that each molecular proportion of hypsulphite required to decolourize the iodine, indicates the previous liberation of one atomic proportion of chlorine from the bleaching powder.

Or that each cubic centimetre of the solution of thiosulphate required by the bleaching powder used indicates the presence of $\frac{35.2}{10000} = 0.00352$ gram of available chlorine in the latter, since each cubic centimetre of the thiosulphate contains $\frac{158}{10000} = 0.0158$ gram of the latter salt.

Several determinations should be made until the student can readily obtain concordant results.

206. The thionic acids. Sulphur also forms a series of acids known as the thionic acids, viz.:—

Dithionic acid		$\text{H}_2\text{S}_2\text{O}_6$
Trithionic acid		$\text{H}_2\text{S}_3\text{O}_6$
Tetrathionic acid		$\text{H}_2\text{S}_4\text{O}_6$ (see 205)
Pentathionic acid		$\text{H}_2\text{S}_5\text{O}_6$
Hexathionic acid		$\text{H}_2\text{S}_6\text{O}_6$.

The details relating to the preparation and properties of these acids must be sought in one of the larger works on chemistry.

207. Sulphur and carbon. Three compounds of sulphur and carbon have been described: a monosulphide (CS), a disulphide (CS_2), and a tricarbon disulphide (C_3S_2). The monosulphide has been described as a combustible gas, produced by treating chloroform (CHCl_3) with sodium sulphide at 180° .

EXPERIMENT 156. To prepare carbon disulphide. Close one end of a piece of combustion tube 500 mm. in length before the blow-pipe. Drop into it some fragments of sulphur, and pack the rest of the tube with fragments of well-made charcoal. Heat the part of the tube which contains the carbon to a cherry-red heat. Then heat the sulphur till it boils, so that its vapour may pass slowly over the carbon, and draw the product through water in a U tube immersed in ice-cold water. If the temperature of the carbon be properly managed, a few drops of crude carbon disulphide will collect under the water in the U tube. Carbon disulphide is prepared on the large scale by a process analogous to that just described.

EXPERIMENT 157. The properties of carbon disulphide. Carbon disulphide is, as we have seen above, heavier than water, and, unless it is very carefully purified, it possesses an exceedingly unpleasant odour.

1. Place a few drops of carbon disulphide in a dish, and notice how rapidly it evaporates. It boils at 46° .

2. Place a few drops of carbon disulphide in a gas cylinder, and allow it to volatilize. Then plunge a hot iron rod (150°) into the cylinder. Its contents will at once take fire.

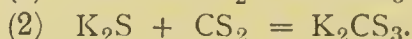
If a detonating cap be ignited in the vapour of carbon disulphide, free from air, the vapour will explode violently*.

* Carbon disulphide is endothermic. Many endothermic compounds may be exploded in a similar manner.

3. Place fragments of sulphur, phosphorus, iodine, and tallow in carbon disulphide. They will dissolve. Carbon disulphide is very useful owing to its power of dissolving such substances.

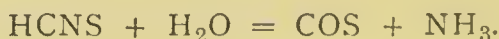
4. Carbon disulphide is very unwholesome, even when it is freely diluted with air, and it may be used as an *insecticide*.

5. A few of the metallic sulphides unite with carbon disulphide, forming a class of salts known as the sulpho-carbonates or thio-carbonates (compare 281). Thus calcium sulphide gives calcium thiocarbonate (CaCS_3):—

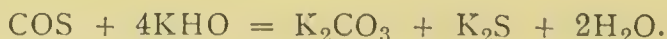


When a thiocarbonate is treated with cold dilute hydrochloric acid a yellow oil, said to be H_2CS_3 , is formed. This is readily resolved into hydrogen sulphide and carbon disulphide. The thiocarbonates of the alkalis are soluble in water.

208. Carbonyl sulphide (COS). If potassium thiocyanate (KCNS) be gently warmed with dilute sulphuric acid, the liberated acid (HCNS) reacts with water, producing ammonia and carbonyl sulphide:—



It is also formed by the combination of sulphur with carbon monoxide. Carbonyl sulphide is a colourless, odourless*, combustible gas which is decomposed at a red heat and reacts with alkalis, producing a mixture of sulphide and carbonate. Thus:—



209. Sulphur and the halogens. Several compounds containing sulphur and halogens are known. Thus sulphur fluoride (SF_2), sulphur monochloride (S_2Cl_2), and sulphur dichloride (SCl_2) all may be prepared by direct combination, and sulphur also combines directly with bromine, probably forming S_2Br_2 and SBr_4 , and with iodine to form S_2I_2 , and possibly also SI_6 . Sulphuryl dichloride (SO_2Cl_2) and chlorosulphonic acid ($\text{SO}_2'\text{Cl}(\text{OH})'$) have already been mentioned in 199.

210. Selenion and its compounds (Se). Atomic weight, 78.6. This element boils at about 670° , and at temperatures near its boiling-

* It is accompanied by other substances when made as described above.

point its vapour density is abnormal (compare sulphur), but at 1420° its vapour density approaches 80, which corresponds to the formula Se_2 .

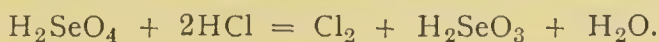
This element occurs free in nature, and is often associated with native sulphur. It is sometimes extracted from the flues of vitriol chambers in works where seleniferous sulphur or pyrites have been roasted.

Selenion occurs in several allotropic forms; (1) A crystalline form, isomorphous with the prismatic sulphur. This may be obtained by evaporating a solution of selenion in carbon disulphide; it melts at *about* 100° , its density is 4.5 ($\text{H}_2\text{O} = 1$), and it readily assumes (2) a plastic form. (3) When fused selenion is cooled quickly, a vitreous variety, soluble in carbon disulphide, is produced ($D = 4.3$); this, if heated to 210° , changes into a grey crystalline mass, which melts at 217° and is insoluble in carbon disulphide. In this form its density is 4.8. Selenion boils at about 670° , and its vapour, when cooled, forms a bright scarlet, powdery deposit. In the crystalline form it conducts electricity.

Selenion burns in air, producing a substance with a characteristic penetrating odour. In excess of oxygen it gives the dioxide (SeO_2), which is a hygroscopic white solid. The dioxide dissolves in water, yielding selenious acid (H_2SeO_3 , or $\text{SeO}(\text{OH})_2$), which may be obtained in crystals.

Selenious acid yields acid and normal salts analogous to the sulphites. It is reduced when it is treated with sulphur dioxide, selenion being deposited. It decomposes carbonates, and even nitrates and chlorides, resembling sulphuric acid in this respect rather than sulphurous acid.

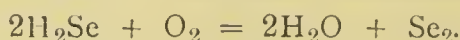
The trioxide of selenion has not yet been isolated, but selenic acid (H_2SeO_4 , or $\text{SeO}_2(\text{OH})_2$) may be made by oxidizing selenious acid by chlorine in the presence of water, and potassium selenate may be produced by fusing selenion with nitre. Selenic acid forms a colourless heavy liquid ($D = 2.6$) which decomposes at its boiling-point; it acts on organic substances much like sulphuric acid (Expt. 152), and forms a series of salts analogous to the sulphates, including some alums. It oxidizes hydrochloric acid, being itself reduced to selenious acid:—



Besides forming the above oxide and oxyacids, selenion is said to yield a compound analogous to carbon disulphide (CSe_2), and several chlorides are known.

Hydrogen selenide or selenuretted hydrogen (H_2Se) is formed when hydrogen mixed with the vapour of selenion is passed through a hot tube, and when iron selenide is treated with hydrogen chloride. It is

an inflammable, colourless gas, which possesses a horrible odour, and is peculiarly irritating to the mucous membrane of the eyes and nose. It is acid to litmus, and its solution is oxidized spontaneously by the air:—

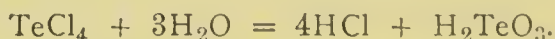


It forms insoluble selenides with many of the metals (compare hydrogen sulphide, Expt. 141, 2).

Selenium may be extracted from flue-dust, in which it is present, by boiling the latter with nitric acid, dissolving the selenic acid thus formed, and treating the solution with hydrochloric acid, whereby the selenic acid is reduced to selenious acid, which is then reduced by means of sulphur dioxide.

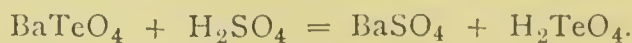
211. Tellurium and its compounds. Atomic weight, 126.6 (see 134). This element is found in a few minerals, associated with gold, silver, lead, and bismuth. It is also present in Japanese sulphur. The element resembles silver in appearance, but it is brittle, and is a bad conductor. It melts at a low red heat, and is volatile. It burns in air with a blue flame, which emits white fumes. It has been met with both in crystals and in the amorphous form.

Oxides of tellurium. Tellurium is said to form three oxides. *Tellurium dioxide* (TeO_2) is prepared by heating tellurous acid to a red heat. This oxide is neutral to litmus and dissolves but slightly in water. Tellurous acid (H_2TeO_3) is prepared by decomposing the tetrachloride of tellurium* with water, when the acid is obtained as a precipitate:—



Tellurous acid is but slightly soluble; it is readily reduced by hydrogen sulphide, zinc, and other reducing agents.

Telluric oxide (TeO_3) and *Telluric acid* (H_2TeO_4). To make telluric acid, tellurous oxide is fused with sodium carbonate, the product is dissolved in water, a little sodium hydroxide added, and chlorine is passed through the solution, which is then neutralized, and mixed with solution of barium chloride. The barium tellurate (BaTeO_4) which is precipitated, is washed, and decomposed with sulphuric acid:—



On evaporating the solution thus obtained, it yields crystals having the composition $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$.

Telluric acid is soluble, becomes anhydrous at 130° , and at higher

* This is made by direct combination.

temperatures yields the trioxide (TeO_3), which, when thus produced, is an insoluble powder. Heat reduces the latter to the dioxide.

Hydrogen telluride. If zinc telluride be dissolved in an acid, a gas (H_2Te) resembling the corresponding compounds of sulphur and selenium is produced. This gas is soluble, acid to litmus, and burns with a blue flame. Its solution precipitates many of the metals.

Under certain conditions tellurium appears to be capable of replacing the hydrogen of some of the acids. Thus it forms a sulphate ($\text{Te}(\text{SO}_4)_2$) and a nitrate.

The student should draw up for himself a table contrasting, first, the properties of the above three elements in the free state, and secondly those of some of their *chief* compounds. This table might take such a form as the one which follows, but it should not be copied from it and might cover considerably more ground.

	<i>Sulphur.</i>	<i>Selenium.</i>	<i>Tellurium.</i>
Atomic weight	32	79	126 (?)
Boiling-point	444.5°	670°	1390° (?)
Density of vapour	Abnormal below 1000°	Abnormal below 1420°	(?)
Specific gravity of solid	2.05	4.8	6.25
	Exists in several forms	Exists in several forms	Crystalline and amorphous forms of tellurium are known
Hydrides	H_2S slightly acidic	H_2Se slightly acidic	H_2Te very slightly acidic
Oxides	SO_2 and SO_3 distinctly acidic	SeO_2 distinctly acidic	TeO_2 and TeO_3 not so distinctly acidic, and TeO_2 basic to some acids
Acids	H_2SO_3 instable and dibasic	H_2SeO_3 stable and dibasic	H_2TeO_3
	H_2SO_4 stable and dibasic	H_2SeO_4 stable and dibasic	H_2TeO_4

212. Other members of the sulphur group of elements.

Group VI in the table on p. 181 includes five other elements besides sulphur, selenion and tellurium, viz. oxygen, chromium, molybdenum, tungsten, and uranium. Sulphur, selenion, and perhaps tellurium, which belong to the odd series 3, 5, and 7, are non-metals, and so is oxygen, but the same can hardly be said of the elements which belong to series 4, 6, 10, and 12, though they form oxides which are more or less acidic in character.

Similar differences will be found to exist between the even series members and the odd series members of other groups, but want of space prevents us from studying this subject minutely at present. An account of chromium will be found at p. 447.

CHAPTER XVI

NITROGEN (N_2): Atomic weight, 13.93. ARGON

213. Nitrogen in atmospheric air. We have seen (66) that when copper is burnt in air, it leaves a colourless, inodorous gas, called nitrogen, which is nearly insoluble in water and does not support combustion.

Nitrogen was first recognized in the expired breath of animals by Rutherford, in 1772; it was afterwards shown to be a component of atmospheric air by Lavoisier, who named it *azote*. The compounds of nitrogen are very numerous; the element is present in the tissues of plants and animals; large quantities are found as nitre (KNO_3), and as Chili saltpetre ($NaNO_3$).

Lord Rayleigh and Professor Ramsay have lately shown us that nitrogen prepared from atmospheric air contains about 1% of a very inactive gas called *argon*, and still more recently Dr. Ramsay has detected minute quantities of other inactive gases in argon.

EXPERIMENT 158. To prepare nitrogen from atmospheric air.

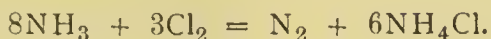
1. Burn phosphorus in a jar of air over water (see Fig. 43).

2. Pass air, previously freed from carbon dioxide, from *B* (Fig. 85) over copper turnings heated to redness in a hard-glass tube *A*. Copper oxide (CuO) will form in *A*, and a mixture containing 99% of nitrogen and 1% of argon will pass through *D* into *E*.

Nitrogen may also be made by passing a mixture of atmospheric air and ammonia (NH_3) over heated copper. If excess of ammonia

be employed the copper will not be oxidized, but water will be formed at the expense of the ammonia.

3. When chlorine is passed into solution of ammonia, nitrogen, free from argon, is liberated :—



But nitrogen is rarely made by this process, for, if excess of chlorine

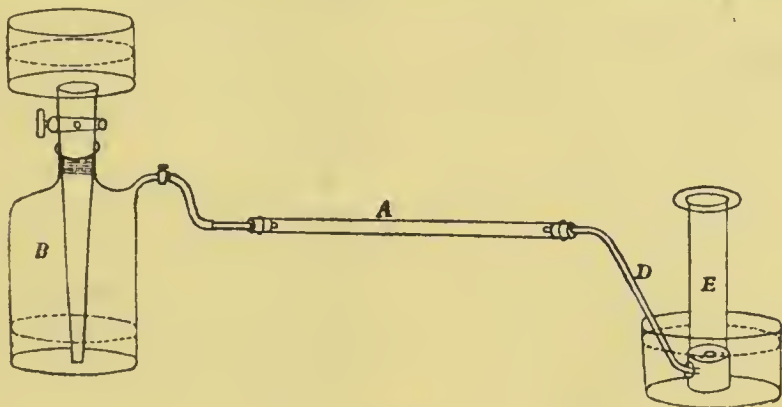
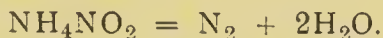


Fig. 85.

be employed, chloride of nitrogen, which is dangerously explosive, will be generated (see 224).

4. When ammonium nitrite (NH_4NO_2) is heated, it splits into water and nitrogen :—



It is difficult to obtain ammonium nitrite, but a solution containing potassium nitrite and ammonium chloride in molecular proportions can be used in its place :—



The product is apt to contain ammonia, and should be washed with acid to remove this impurity.

214. Some properties of nitrogen. Physical properties. Density 14 ($\text{H} = 1$). It is less soluble in water than oxygen, and is colourless and odourless. Nitrogen has been condensed to a colourless liquid which is lighter than water. Its critical point is -146° and its critical pressure 35 atmospheres. It boils at -194.4° in air and freezes at -214° .

EXPERIMENT 159. To study the chemical properties of nitrogen. 1. Pass a slow current of nitrogen over magnesium turnings heated to dull redness in *A* (Fig. 85). The metal will lose its metallic

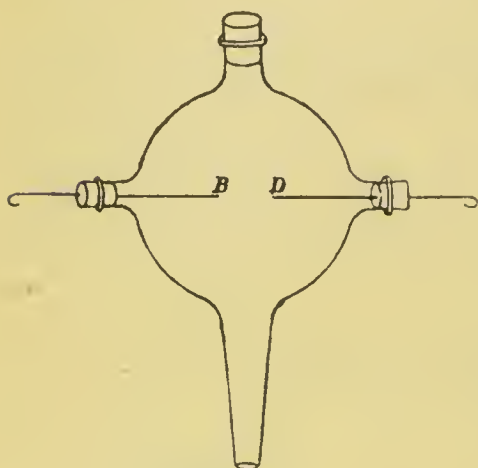


Fig. 86.

lustre and be converted into magnesium nitride (Mg_3N_2). Add a little water to some of the nitride. Ammonia will be evolved (see 217).

Nitrogen also combines directly with silicon, boron, oxygen, and hydrogen, and with a few other elements.

2. Add a little oxygen to the air in a globe (Fig. 86), close its open ends with corks, and pass sparks from an induction coil between the electrodes *B D*. The mixture will gradually acquire a yellow colour and a nitrous

smell, owing to the formation of nitric peroxide (N_2O_4). Nitrogen can be made to combine with hydrogen, to a small extent, under the influence of the silent discharge of electricity (Expt. 99).

215. Nitrogen in its relations to plants and animals.

Although free nitrogen combines directly with but few of the other elements, and is, on the whole, a very inactive substance, it enters into the formation of many interesting compounds, which play an important part in the life processes of both plants and animals (306). The former are believed to obtain their nitrogen, mainly in the form of nitrates, from the soil, but certain plants belonging to the pea-tribe (*leguminosæ*) are capable of utilizing atmospheric nitrogen. This remarkable power seems to be connected with the presence of certain nodules, which swarm with micro-organisms, on the roots of the plants. The organisms in these nodules are supposed to play an important part in the processes by which the plants accumulate atmospheric nitrogen, and they are said to live in *symbiosis* with the plants. Animals, on the other hand, depend upon the plants for their supply of nitrogen, as well as for their carbon, and when the former has served its purpose in the animal organism, it is excreted, mostly in the form of *urea* ($\text{N}_2\text{H}_4\text{CO}$), and after undergoing further transformations under the

influence of various micro-organisms is presently reconverted into nitric acid, and is then ready to nourish a new generation of vegetables.

216. Argon. In the year 1894, Lord Rayleigh observed that the density of nitrogen prepared from air is slightly greater than the density of nitrogen made from compounds such as ammonium nitrite, and he and Professor Ramsay afterwards succeeded in isolating a new and very inert gas, which they have named *argon*.

Argon may be obtained by passing atmospheric nitrogen slowly over turnings of magnesium heated to dull redness in a hard glass tube *A* (Fig. 85), until the density of the gas ceases to increase. It may be isolated also by sparking a mixture of air and oxygen collected over an alkaline solution; the alkali absorbs the oxides of nitrogen as they are formed, and leaves the argon. 7900 c.c. of air treated in this way gave 65 c.c. of the new gas. Thus prepared it contains three other gases, neon, krypton, and xenon in very small proportions. Argon is colourless and odourless, like nitrogen, but it is rather more soluble in water. Its density is about 20 ($H = 1$), it has been liquefied and frozen. From the velocity with which sound is propagated in argon it is concluded that its molecules are monatomic like those of mercury, therefore its atomic weight, if it be an element, is about 40.

Argon is a remarkably inert gas, and may be recognized, most conveniently, by its spectrum. When it is submitted to the electric discharge in a vacuum tube at a pressure of about 3 mm., it gives a red glow, and its spectrum (see 336), which consists of many lines spread over the whole field, exhibits two characteristic lines at the extreme red end. Under special conditions argon gives a blue glow and a second spectrum.

217. Ammonia and its preparation (NH_3). Nitrogen and hydrogen do not readily combine, but minute amounts of ammonia may be made by submitting a mixture of the two gases to the action of the silent discharge of electricity.

EXPERIMENT 160. Methods of generating ammonia. 1. Add a little water to some magnesium nitride. A pungent, alkaline gas, resembling that given off by smelling-salts, will be evolved, and a white alkaline solid, magnesium oxide, will remain :—



Other nitrides, e.g. silicon nitride, behave similarly with water.

2. Nascent hydrogen reduces alkaline solutions of nitrates and nitrites, producing ammonia. Dissolve a crystal of nitre in a little solution of potash, add a small piece of aluminium foil, and apply heat, if necessary. The liquid will soon acquire the odour of ammonia, owing to the reduction of the nitrate by the hydrogen liberated from the alkali by the aluminium.

3. Heat some fragments of coal in a glass tube laid horizontally in a small furnace, and convey the volatile products to a well-cooled U tube. You will probably be able to detect the odour of ammonia in the condensed liquid.

A great deal of ammonia is made by distilling coal in gas-works, and elsewhere (see 303). Ammonia is also formed when horn or bones are distilled, and a solution containing ammonia thus made was long used under the name of *spirit of hartshorn*. A salt called *sal-ammoniac* is said to have been made formerly, in Egypt, in the neighbourhood of a temple to Jupiter Ammon, and it is supposed that the name ammonia is derived from this circumstance.

When nitrogenous organic matter undergoes putrefaction, most of its nitrogen is given off as ammonia, consequently this gas may often be detected, by its odour, in ill-ventilated stables; and it is believed that the greater part of the nitrogen in the tissues of plants and animals is ultimately returned to the air in the form of the ammonia produced in this way.

Ammonia was first recognized as a distinct form of matter by Priestley, in 1774.

EXPERIMENT 161. To prepare ammonia gas. Warm 4 parts of sal-ammoniac (NH_4Cl) with about 3 parts of slaked lime*, and a little water, in a flask. Ammonia will be given off, and may be recognized by its pungent smell:—



Fill the flask used for a previous experiment (Fig. 62) with ammonia by upward displacement, and open its end under water. The water will dissolve this gas as rapidly as it dissolves hydrochloric acid. Ammonia must therefore be collected by displacement of air, or over quicksilver.

Liquid ammonia was first made by Faraday, by passing the dry gas through a strong tube (Fig. 87), which contained a quantity of

* Any other alkali will do as well.

silver chloride in one arm *A*. When the silver chloride was saturated with the gas, $2\text{AgCl}, 3\text{NH}_3$ being formed, the tube was sealed at *C* and *C*. Its empty limb *B* was next placed in a freezing mixture, and the other limb *A* was cautiously heated. The ammonia was then given off and liquefied by its own pressure.

218. Physical properties of ammonia.

Liquid ammonia boils at about -34° , and dissolves such substances as sulphur, phosphorus, and iodine. If an open vessel containing it be immersed in

water, the ammonia evaporates rapidly, and the heat absorbed causes ice to form. The ice-making machine of M. Carré depends on this fact. M. Carré used, however, a strong solution of ammonia in water in place of the liquefied gas. Ammonia is sometimes called 'volatile alkali' to distinguish it from the non-volatile or fixed alkalis, potash and soda. Ammonia is much lighter than air, its density being only 0.589 (Air = 1), and hence we must collect it, as we do hydrogen, by upward displacement of air. If it be cooled by ether and carbon dioxide it condenses to a crystalline solid.

EXPERIMENT 162. To make solution of ammonia (NH_3) or ammonium hydroxide (NH_4HO). Set up the apparatus used for making solution of hydrochloric acid (Fig. 63), charge the generator with ammonium chloride and slaked lime, and pass the ammonia formed through water in the wash bottles.

Owing to the difficulty of storing large quantities of a gas, ammonia is usually kept in the laboratory in the form of a strong aqueous solution. This solution * may contain about 1150 c.c. of the gas in each cubic centimetre of water, but the solutions ordinarily met with are made at higher temperatures and contain smaller proportions than this. If the density of a solution of ammonia is known, its strength can be found by consulting a table drawn up for the purpose. The following table gives the densities and strengths of solutions of ammonia at 14° , but much fuller details may be found in some of the larger works on chemistry:—

Density	% NH_3	Density	% NH_3
0.8844	36.0	0.8976	30.0
0.8907	33.0	0.9106	25.0

* If made at 0° .

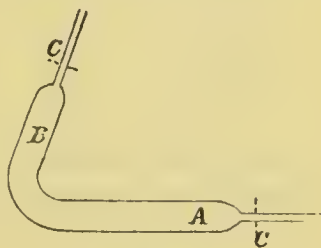


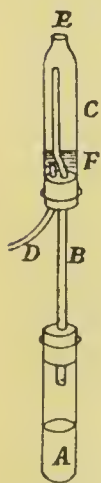
Fig. 87.

<i>Density</i>	<i>% NH₃</i>	<i>Density</i>	<i>% NH₃</i>
0.9251	20.0	0.9915	2.0
0.9414	15.0	0.9959	1.0
0.9593	10.0	0.9983	0.4
0.9790	5.0	0.9991	0.2
0.9873	3.0		

219. Some chemical properties, and the composition of ammonia. EXPERIMENT 163. To study the chemical properties of ammonia gas and ammonia solution. 1. Mix a jar of ammonia, dried by the action of quicklime, with a jar of hydrochloric acid. Dense white fumes of ammonium chloride (NH₄Cl) will be formed :—



2. Plunge a lighted taper into a jar of ammonia. The taper will be extinguished, and the gas, in spite of its richness in hydrogen, will not be ignited.



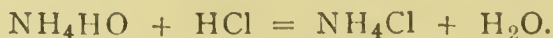
3. Heat some strong solution of ammonia in a tube *A*, and convey the gas evolved into tube *C* by *B*. At the same time pass oxygen by *D* through the glass wool *F* into *C*, and ignite the mixture as it escapes at *E*. The ammonia will burn with a peculiar greenish-yellow flame. The products of its combustion are water and nitrogen, unless excess of oxygen be employed, in which case it is said that some nitrite of ammonium is formed.

4. Hold a drop of a solution of copper sulphate, on a glass rod, in ammonia. It will acquire a fine blue colour (378).

5. Neutralize some dilute solution of sulphuric acid, or of hydrochloric acid, with some solution of ammonia, and cautiously concentrate the product. You will obtain crystals of sulphate or chloride of ammonium :—



or possibly :—

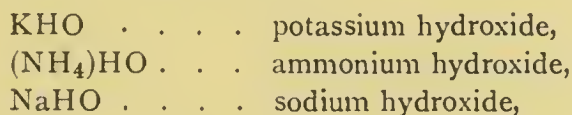


6. Add solution of ammonia to some recently precipitated chloride, bromide, iodide, and phosphate of silver, and notice that these salts with the exception of the iodide, are freely dissolved.

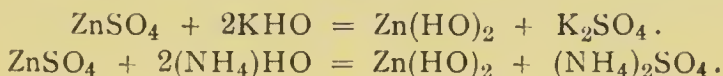
Some metallic oxides, e. g. CuO and Ag₂O, are also dissolved by solution of ammonia.

7. Add some solution of ammonia gradually to solutions containing ferric chloride, ferrous sulphate, zinc sulphate, manganese sulphate, and alum. In every case, the metal will be precipitated as hydroxide. Thus, ferric chloride will give ferric hydroxide ($\text{Fe}_2(\text{HO})_6$ or $\text{Fe}(\text{HO})_3$); alum will give aluminic hydroxide ($\text{Al}_2(\text{HO})_6$ or $\text{Al}(\text{HO})_3$); and zinc salts will give zinc hydroxide ($\text{Zn}(\text{HO})_2$).

The formation of these compounds may be accounted for by supposing that solution of ammonia contains a hydroxide (NH_4HO) in which the compound radicle *ammonium* (NH_4) plays a similar part to that of potassium and sodium in the hydroxides of those metals, as suggested by the following formulæ :—



and that this substance reacts like potash and soda with metallic salts. Thus :—



As we shall learn from a subsequent experiment, ammonium hydroxide, if it exists, is so instable that ammonia may be conveniently prepared by warming strong solution of ammonia.

EXPERIMENT 164. To find the composition of ammonia. Collect some ammonia free from air, and dried by means of quicklime, over quicksilver in a eudiometer, and find its volume under standard conditions. Pass a rapid discharge of sparks from an induction coil through the gas. It will soon be seen to expand. Continue to spark the gas until its volume becomes constant; then find its new volume at 0° and 760 mm. as before.

Since ammonia may be obtained by the direct union of hydrogen and nitrogen, we may assume that the sparks decompose it into these two gases.

Add about half its volume of oxygen to the expanded gas, and note the volume of the mixture at 0° and 760 mm. Explode it by a spark of electricity, taking the usual precautions, and note the volume of the contracted gas.

Two-thirds of the contraction must be due to hydrogen, and one-third to oxygen (Expt. 54).

Now deduct the volume of the hydrogen from the volume of the

mixture of hydrogen and nitrogen, or absorb the excess of oxygen with alkaline pyrogallate, and measure the residual nitrogen.

Example. Let us suppose that the following data were obtained:—

1. Volume of ammonia taken for analysis . . . 5.2 c.c.
2. Volume of the hydrogen and nitrogen . . . 10.35 c.c.
3. Volume of the hydrogen, nitrogen, and oxygen . 20.0 c.c.
4. Volume after exploding the mixture . . . 8.3 c.c.
5. Residue from pyrogallate, viz. nitrogen . . . 2.61 c.c.

The contraction which occurred when the gases were exploded amounted to 11.7 c.c. (20.0 – 8.3).

$\therefore 11.7 \times \frac{2}{3} = 7.8$ c.c. of hydrogen were obtained from 5.2 c.c. of ammonia.

And 2.61 c.c. of nitrogen remained.

$\therefore 7.8$ c.c. of hydrogen and 2.61 c.c. of nitrogen were obtained from 5.2 c.c. of ammonia.

The respective densities of the gases are approximately 1, 14, and 8.5. Therefore the proportions by weight corresponding to these volumes are:—

Hydrogen	.	.	7.8	$\times$	1	=	7.8
Nitrogen	.	.	2.61	$\times$	14	=	36.5
Ammonia	.	.	5.2	$\times$	8.5	=	44.2

Or 44.2 parts of ammonia when decomposed produce 36.5 parts of nitrogen and 7.8 parts of hydrogen.

EXPERIMENT 165. To detect ammonia in its compounds. The hydroxide and the carbonate of ammonium slowly decompose at ordinary temperatures, giving off ammonia, and therefore may be recognized by their odour; but if other ammonium salts, e.g. the chloride or sulphate, be examined, they will be found to be quite free from the odour of ammonia.

Warm a small portion of one of these salts with some slaked lime, or with sodium hydroxide. You will at once recognize the odour of ammonia.

EXPERIMENT 166. Nessler's test for ammonia. Dissolve 10 grams of potassium iodide in 40 c.c. of distilled water, add a saturated solution of mercuric chloride until a permanent precipitate of mercuric iodide just begins to form, then a cold solution containing 25 grams of caustic potash in 25 c.c. of water, and mix well. Next add a few more drops of solution of mercuric chloride till a permanent precipitate

forms, dilute to 160 c.c., mix well, allow the precipitate to settle, and decant the clear liquid. This is 'Nessler solution.' It contains, with alkali, the elements of the salt $\text{HgI}_2, 2\text{KI}$.

Dissolve 1.573 grams of ammonium chloride in a litre of water, and dilute 100 c.c. of the product to 1 litre. Each cubic centimetre of this solution will contain 0.00005 gram of ammonia. Label it 'Solution A.'

Place half a cubic centimetre of 'A,' diluted to 50 c.c. with water, in a thin glass cylinder standing on a sheet of white paper, add 2 c.c. of the Nessler solution, and mix well. After five minutes observe the brownish-yellow tint acquired by the water.

Repeat the experiment, using twice as much of solution A. Notice that the tint produced is decidedly deeper than before.

Obtain a very dilute solution of ammonia of known strength from your teacher, and endeavour to find the amount of ammonia in a litre of it, in the following manner :—

Add Nessler solution as before to 50 c.c. of the liquid to be tested, and note the tint produced. Then prepare a solution of ammonia of suitable and known strength from solution A. Add Nessler solution to this, and compare the tint produced with that given by the water you are examining. If the two tints do not match, prepare a fresh solution of ammonia from A, and add Nessler solution, &c., as before, repeating the process until a match is obtained*.

Then, since you know the strength of one of these solutions, you also know the strength of the other.

EXPERIMENT 167. The effect of heat on compounds of ammonium. Dissociation. Heat a small fragment of sal-ammoniac in a test tube. It will sublime, and after a second or two a faint odour of ammonia may be detected at the mouth of the test tube, which shows that decomposition, or dissociation, has occurred.

220. Dissociation of compounds of ammonia. The compounds of ammonium exhibit abnormal vapour densities (see 197, 198).

If a molecule of ammonia (NH_3) unite with a molecule of hydrochloric acid (HCl), the simplest formula we can adopt for the compound produced is $\text{NH}_4\text{Cl}^\dagger$. The molecular weight of a compound

* Nesslerizing can be done most successfully if the solution of ammonia is very dilute, as intense colourations cannot be compared successfully.

† If it be admitted that the formulæ adopted for ammonia and hydrogen chloride are correct.

having this formula would be $14 + 4 + 35.2 = 53.2$, and therefore its vapour density would be 26.6, i. e. $\frac{53.2}{2}$ (see 91). But the density of ammonium chloride as determined experimentally is found to be about 14*.

This fact, supported as it was by the abnormal vapour density of sulphuric acid, at one time led chemists to doubt the validity of Avogadro's hypothesis. The phenomenon can be explained, however, by supposing that each molecule of ammonium chloride splits into a molecule of ammonia and one of hydrogen chloride when it volatilizes, and that the products of the change reunite when they are cooled:—



for the density of such a mixture of ammonia and hydrochloric acid would be the mean of the sum of the densities of its constituents, i. e. $\frac{8.5 + 18.1}{2} = 13.3$.

The correctness of this hypothesis may be tested by the following elegant experiment, which we owe to Professor Tilden.

EXPERIMENT 168. To ascertain whether an ammonium salt dissociates when it is heated. Fix a piece of porous pipe stem *B* and two short glass tubes *C C* into a larger glass tube *A*. Place some sal-ammoniac inside *A*. Connect one end of *B* with a gas-holder filled with air, or with a pair of bellows. Heat the chloride till it

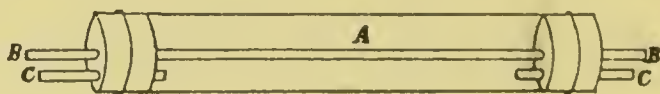


Fig. 89.

sublimes, and send a stream of air through *B*. Ammonia mixed with air will escape from *B* (it may be detected by the usual tests), because it is less dense than hydrogen chloride, and hence diffuses more rapidly (129). If the contents of *A* be examined at the end of the experiment, free acid will be found to be present. Now it is only the constituents of mixtures that can be separated by diffusion. Hence the ammonium chloride must have broken up into a mixture of ammonia and hydrochloric acid.

The ammonium salts are more fully described at p. 408.

* Dr. Brereton Baker finds that the vapour density of this salt is normal if it be perfectly dry.

221. Hydrazine (Diamidogen) (N_2H_4). This interesting compound is a colourless, volatile, liquid which freezes at 0° . It is a powerful base, forming such compounds as $N_2H_4 \cdot HCl$, and $N_2H_4 \cdot 2HCl$. It is difficult to obtain in the free state, and can only be manipulated conveniently in vessels of silver or platinum. It is a powerful reducing agent. Its hydroxide ($NH_2 \cdot NH_3 \cdot (OH)$) corrodes glass, cork, and india-rubber, possesses a caustic taste, and absorbs carbon dioxide like the caustic alkalis.

A molecule of hydrazine may be considered to be derived from one of ammonia (NH_3), by replacing an atom of hydrogen by the radicle amidogen (NH_2), therefore its formula may be written $NH_2 \cdot NH_2$ or $\begin{Bmatrix} NH_2 \\ NH_2 \end{Bmatrix}$. Each amidogen group reacts with acids like ammonia, and thus we get the two classes of salts mentioned above, e.g. $\begin{Bmatrix} NH_3Cl \\ NH_2 \end{Bmatrix}$ $\begin{Bmatrix} NH_3Cl \\ NH_3Cl \end{Bmatrix}$ and the hydroxide $\begin{Bmatrix} NH_3OH \\ NH_2 \end{Bmatrix}$.

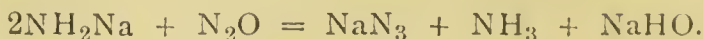
222. Hydroxylamine (NH_2OH). The hydrochloride of this derivative of ammonia is formed when nitric oxide (NO) is passed through flasks in which tin is dissolving in hydrochloric acid, in the presence of a little tetrachloride of platinum ($PtCl_4$). If the tin be precipitated by hydrogen sulphide, and the filtrate evaporated to dryness and extracted with absolute alcohol, a solution is obtained from which ether precipitates hydroxylamine hydrochloride.

Hydroxylamine is a colourless crystalline solid which melts at about 33° . When heated it is very apt to explode. It inflames in chlorine, and is attacked by the other halogens. It is oxidized by the air, nitrous acid and ammonia being among the products. It is altogether a very instable substance possessing considerable reducing power.

Hydroxylamine is basic, uniting with acids to form such salts as $NH_2(OH)HCl$. The hydrochloride is a crystalline solid, which, when strongly heated, decomposes, with great evolution of fumes.

223. Azoimide, hydrazoic acid or hydrogen nitride (N_3H). This remarkable substance, unlike the other hydrides of nitrogen, is acidic. It may be obtained by passing ammonia over half a gram of sodium heated cautiously in a porcelain boat in a glass tube, until the sodium is converted into an amide ($NaNH_2$), and then heating the sodamide to 200° in a current of dry nitrous

oxide. This converts the sodamide into the sodium salt of hydrazoic acid (NNa_3):—



If the product be distilled with excess of weak sulphuric acid, a dilute solution of hydrazoic acid will be obtained.

Hydrazoic acid has an unpleasant smell and an acid reaction with litmus. The pure acid boils at 37° , and explodes if it be heated, and sometimes even if it be not heated, with a blue flash. Its solution dissolves many metals such as iron and copper*, hydrogen being evolved. It is liberated from its salts by dilute sulphuric acid. The following are the formulæ of some of its metallic derivatives:—

BaN_6	.	.	.	Barium nitride.
NaN_3	.	.	.	Sodium nitride.
NH_4N_3 or N_4H_4	.	.	.	Ammonium nitride.
AgN_3	.	.	.	Silver nitride.

They are mostly crystalline, soluble in water, and violently explosive if heated, but the sodium salt is more stable.

Owing to its explosive character this substance and its derivatives should not be prepared by young students.

224. Nitrogen and the halogens. Nitrogen and chlorine.

EXPERIMENT 169. To prepare nitrogen chloride. (Not to be done by the student.) Place some solution of ammonium chloride, saturated at 35° , in a basin *A* (Fig. 90), and also in a cylinder *B*, which must be closed at its lower end with a sheet of parchment *C*. Pour a few drops of turpentine on the surface of the solution in *B*. Connect the platinum plate *D* with the negative electrode of a battery of galvanic cells, and a second plate *E* with the positive electrode. Drops of a yellow liquid will rise through the solution in *B* and explode as they come into contact with the turpentine.

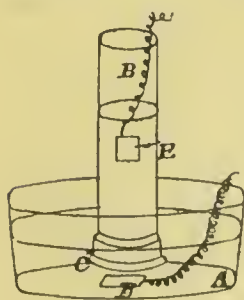


Fig. 90.

These drops consist of nitrogen chloride, a yellowish oil possessing a sharp, irritating smell, which explodes violently when brought into contact with grease or turpentine, and when its vapour is heated. It is soluble in benzene and in chloroform, giving solutions which can be handled safely. It reacts violently with ammonia, giving nitrogen and hydrogen chloride:— $\text{NH}_3 + \text{NCl}_3 = \text{N}_2 + 3\text{HCl}$.

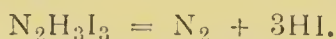
* It is said also to attack gold and platinum.

Hence nitrogen can be prepared safely by the interaction of chlorine and ammonia, provided that the latter is present in excess (see 213), but when all the ammonia is destroyed further addition of chlorine produces the dangerous chloride of nitrogen.

Chloride of nitrogen is also formed when hypochlorous acid acts upon ammonium chloride.

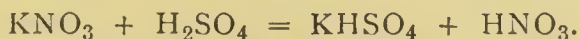
It is doubtful whether nitrogen bromide has ever been isolated.

EXPERIMENT 170. Nitrogen iodide. Add strong solution of ammonia in excess to a few cubic centimetres of a solution of potassium iodide containing a decigram of iodine. Collect the black precipitate in very small portions on filter papers and allow it to dry. Observe its colour, and notice that it explodes violently on being struck, liberating nitrogen, iodine, and hydrogen iodide. This substance has long been known as nitrogen iodide; it can be obtained in small ruby red crystals. It has the composition $N_2H_3I_3$, and probably the constitution $H_3N=NI_3$. In sunlight it decomposes, yielding nitrogen and hydrogen iodide, a reaction which will recall the interaction of nitrogen chloride and ammonia:—

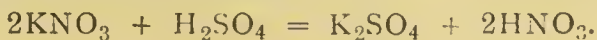


225. Nitric acid. Nitric acid does not occur free in nature, but nitrates of sodium, potassium, magnesium and calcium exist in the soil, and in the juices of plants. Large deposits of nitrate of sodium are found in Chili, and nitrate of potassium is extracted from the soil in India, and some other hot countries, where it often appears as a saline efflorescence. Nitre may be prepared artificially from nitrogenous refuse (see also 362).

EXPERIMENT 171. To prepare nitric acid from a nitrate. Heat forty or fifty grams of nitre with an equal weight of strong sulphuric acid in a retort, and introduce the neck of the retort into the mouth of a well-cooled flask (Fig. 14). A pale straw-coloured liquid, nitric acid, will distil over. The change which occurs corresponds to the following equation:—



On the manufacturing scale a greater proportion of nitre is employed and the materials are heated in an iron retort. The *by-product* then consists of the salt K_2SO_4 , which could not be removed from a glass retort so easily as the acid sulphate:—



Chili saltpetre may be used in place of nitre, but the acid produced may contain traces of iodine. [Why? see 163.]

Nitric acid, as ordinarily prepared, contains about 68 per cent. of real nitric acid (HNO_3), but an acid containing 95 or 96 per cent. may be made by redistilling the weaker acid with an equal volume of oil of vitriol, and collecting apart the first portions of the distillate. Nitric acid usually holds oxides of nitrogen in solution; if these are removed by blowing air through the strongest acid, it forms a colourless liquid which boils at 86° , and has the density 1.530 ($\text{H}_2\text{O}=1$) at 15° .

If a concentrated solution of nitric acid is boiled, its boiling-point gradually rises to 120.5° , at 760 mm.; the residue, which contains 68 per cent. of real acid, was formerly supposed to consist of a definite hydrate, but the composition and boiling-point of the product is now known to depend upon the pressure at which it is distilled*.

It is doubtful whether the pure acid (HNO_3) has been prepared, but Sir Henry Roscoe has obtained specimens containing 99.5 to 99.8 per cent. of HNO_3 .

EXPERIMENT 172. Some properties of nitric acid. 1. Dip blue litmus paper in some well-diluted nitric acid. The litmus will be reddened.

2. Neutralize some potassium carbonate with moderately dilute nitric acid; evaporate and cool the solution. Crystals of nitre (KNO_3) will form:—



3. Add a few drops of strong nitric acid to some indigo. The latter will be bleached.

4. Add a little strong nitric acid to solution of iodide of potassium. Iodine will be liberated as it is by chlorine and other powerful oxidizers.

5. Place a feather, some white silk, or other animal tissue, in strong nitric acid. It will be stained yellow.

226. Nitric acid an oxidizing agent. 1. Throw warm nitric acid on warm powdered charcoal. Violent action will ensue, red fumes will be given off, and the carbon may ignite.

2. Warm a little finely powdered iron sulphide (FeS) with strong nitric acid, dilute the solution, and add some solution of barium chloride. A precipitate of barium sulphate (BaSO_4) will fall.

3. Pour some nitric acid on about a gram of red phosphorus, and, if necessary, apply heat. Violent action will occur, red fumes being

* Compare hydrochloric acid, 143.

produced copiously, owing to the reduction of the nitric acid. Evaporate the product till a glassy solid remains. This residue is metaphosphoric acid (HPO_3).

4. Dissolve a few crystals of ferrous sulphate in water, add a little sulphuric acid, then some nitric acid, and apply heat. Nitrous fumes, which consist largely of nitric oxide (NO), will be evolved.

Test the product for ferrous and ferric salts (see 499). The latter alone will be found:—



227. The action of nitric acid with the metals. Free hydrogen is not often produced when metals are dissolved in nitric acid, but some other gas, or gases, are generated by the reduction of the acid. The nature of these gases depends upon the metal dissolved, the state of concentration of the acid, and on the temperature at which the experiment is made. The following experiments will illustrate this intricate subject:—

Warm some strong nitric acid with some granulated tin in a very capacious flask. Dense red nitrous fumes will be evolved, and an oxide of tin (SnO_2) will remain. The fumes are largely composed of nitrogen peroxide (237).

Cover some granulated zinc with some dilute nitric acid containing about 1 per cent. of real acid, warm them gently, and stand them aside for a few hours. Then warm the solution with excess of alkali. Ammonia will be evolved, for ammonium nitrate (NH_4NO_3) has been formed by the reduction of part of the nitric acid (HNO_3).

Pour some well diluted nitric acid on some magnesium turnings. Hydrogen, in a more or less pure state, will be given off, if the acid is sufficiently diluted.

Since the nature of the products of the action of nitric acid on a metal depends on such conditions as the strength of the acid, the nature of the metal, and the temperature at which they act, it is not usually practicable to represent the exact change that occurs, in any given case, by an equation. In the case of copper and properly diluted nitric acid, however, nitric oxide is the chief product. In this case the change may be represented as follows:—



228. EXPERIMENT 173. Tests for nitric acid. Several of the properties of nitric acid, e. g. its action on feathers and on copper, may be employed as tests.

Dissolve a small fragment of nitre in some water, and add a few drops of a solution of sulphate of iron. Then pour down the side of the test tube a few drops of strong sulphuric acid, so that it forms a layer beneath the lighter liquid. A brown ring will soon form at the line of junction between the acid and the lighter liquid. This dark ring contains a compound of nitric oxide (NO) with ferrous sulphate. The nitric oxide is produced by the oxidation of part of the ferrous salt by nitric acid.

229. Nitration—gun-cotton—nitro-glycerin. Nitric acid often acts on organic substances in such a manner as to replace one or more atoms of hydrogen by the group NO_2 . Mix some strong nitric acid with an equal volume of strong sulphuric acid, immerse some cotton-wool in the mixture, remove the cotton after a few minutes, wash away excess of acid with water, and dry the product. Then apply a light to it. It will disappear with a flash, for it has been converted into a kind of gun-cotton by the replacement of part of the hydrogen of the cellulose $((\text{C}_6\text{H}_{10}\text{O}_5)_n)$ by NO_2 . Various substances of this kind have been prepared, gun-cotton being *cellulose hexa-nitrate* $(\text{C}_{12}\text{H}_{14}(\text{NO}_3)_6\text{O}_4)$.

Another interesting compound of the same class is the explosive 'nitro-glycerin,' or *trinitro-glycerin*, which is produced in a somewhat similar manner from glycerol $(\text{C}_3\text{H}_5(\text{OH})_3)$; and some of the modern smokeless powders are mixtures containing both these substances, usually with other constituents *.

Nitrobenzene. Add some benzene (C_6H_6) very gradually to a cold mixture of nitric acid and sulphuric acid in equal proportions. Pour the product into a flask of cold water; a yellowish heavy oil with an odour somewhat like that of essence of almonds will separate. This contains nitrobenzene or artificial oil of almonds $(\text{C}_6\text{H}_5(\text{NO}_2))$.

If some nitrobenzene be brought in contact with a flame it will be found difficult to ignite. It is used for scenting soap and for making aniline dyes.

230. Explosives. The chief explosives may be arranged in two classes, viz. explosive mixtures like gunpowder, and explosive compounds like nitro-glycerin.

Gunpowder of the old-fashioned kind is a mixture of combustible substances, carbon and sulphur, with a supporter of combustion, nitre

* Dynamite consists of a silicious earth mixed to a pasty mass with nitro-glycerin.

(KNO_3). Its action may be said to depend on the fact that the oxidation of the former substances by the latter produces, somewhat suddenly, great volumes of highly heated gases, so that if the powder be enclosed in a small space, as in a rifle barrel, at the moment of its ignition a correspondingly high pressure is developed. The action of the older kind of gunpowder is not so sudden as that of some other explosives. The former is known as a 'low explosive.' It gives out several hundred times its own volume of gases when burnt; these consist largely of carbon dioxide, carbon monoxide, and nitrogen.

Nitro-glycerin and gun-cotton. These substances are obtained by the action of concentrated nitric acid on glycerin and cellulose respectively. The nitric acid so acts on the glycerin and cellulose as to replace part of their hydrogen by the group NO_2 . In the case of glycerin ($\text{C}_3\text{H}_5(\text{HO})_3$), for example, the compound $\text{C}_3\text{H}_5(\text{NO}_2)_3$ is formed. When an explosive of this second class is detonated, great volumes of very hot gases are produced, and the change takes place far more suddenly than in the case of gunpowder. Hence their action is very intense, but more local than in the other case; and they are known as 'high explosives.' This characteristic has made it difficult to utilize high explosives as propulsive agents for rifles and artillery, but the difficulty has been overcome of late years by the employment of suitable mixtures, and the addition of other substances which modify their action.

Explosive mixtures of gases, such as mixtures of coal gas and air, are chiefly used in gas engines. We have already met with an explosive gas in chlorine peroxide (154).

231. Basicity of nitric acid. When nitric acid is mixed with potash or soda in various proportions only one salt is formed, and this salt contains no hydrogen. We cannot replace the hydrogen of nitric acid at two stages, as we can that of sulphuric acid. Therefore we conclude that a molecule of nitric acid contains but a single atom of hydrogen, or that nitric acid is monobasic.

232. Nitrates. EXPERIMENT 174. **Some properties of nitrates.** 1. Warm a nitrate with strong sulphuric acid. Acid fumes (HNO_3) accompanied by a little red oxide of nitrogen will be evolved.

2. Melt a little nitre in a dish, add sulphur in very small fragments, one by one, and test the product, after cooling it, for a sulphate.

3. Drop small fragments of carbon cautiously into melted nitre.

They will be consumed rapidly. Test the product for carbonate by adding some free acid to it.

4. Nitrates are reduced to ammonia by nascent hydrogen in the presence of alkali (Expt 160, 2).

5. Heat some copper nitrate strongly in a dish. Red fumes (N_2O_4) will escape, leaving a residue of black oxide of copper (CuO):—



6. Heat magnesium nitrate. A similar result will be obtained, a white alkaline residue of magnesium oxide (MgO), soluble in acids, being left.

7. Most nitrates are converted into oxides by heat, but the nitrates of metals which form instable oxides yield the metal. Heat some nitrate of mercury cautiously till a red residue of mercuric oxide remains, then heat this more strongly. It will produce oxygen and mercury, or, if any nitrate is still present, red nitrous fumes mixed with oxygen and mercury.

Heat a little nitrate of silver. Notice that red fumes are given off, and that a residue of finely divided silver remains.

8. Nitrates of the alkali metals give nitrites. Heat a little nitre strongly. Oxygen will be evolved. Dissolve the residue in water, and warm the solution with dilute sulphuric acid; or add to it a mixture of dilute sulphuric acid, starch water, and iodide of potassium. In the former case a red gas will be produced; in the latter iodide of starch will be formed (see nitrites, 236).

233. The oxides of nitrogen. There are no less than five oxides of nitrogen. These oxides illustrate well the law of multiple combination (80), as will be gathered from the following table:—

<i>Name.</i>	<i>Proportion of Nitrogen.</i>	<i>Proportion of Oxygen.</i>
Nitrous oxide (N_2O) (nitrogen monoxide)	14 parts	8 parts
Nitric oxide (NO)	14 "	16 = (8 × 2) "
Nitrogen trioxide (N_2O_3) (nitrous anhydride)	14 "	24 = (8 × 3) "
Nitric peroxide (N_2O_4) (nitrogen tetroxide)	14 "	32 = (8 × 4) "
Nitrogen pentoxide (N_2O_5) (nitric anhydride)	14 "	40 = (8 × 5) "

234. Nitrogen pentoxide or nitric anhydride (N_2O_5 , or N_4O_{10}). When nitric acid, free from nitrous acid, is cautiously distilled with phosphoric anhydride (P_4O_{10}), a white crystalline solid (N_2O_5) volatilizes, and metaphosphoric acid (HPO_3) remains in the retort :—



The same oxide is formed when dry chlorine is passed over dry silver nitrate :—



Nitric anhydride forms beautiful crystals, which melt at 30° and boil easily, but which are dangerously apt to explode, and cannot be long preserved. It is a violent oxidizing agent. The formula N_2O_5 agrees most simply with its action with water, which produces nitric acid :—



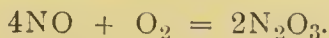
but its vapour density is not known.

235. Nitrogen trioxide or nitrous anhydride (N_2O_3). **EXPERIMENT 175.** Preparation and properties of nitrous anhydride. Warm arsenious oxide (As_4O_6) with nitric acid *. Arsenic acid (H_3AsO_4) will be formed, and red nitrous fumes given off :—



Cool these fumes by means of ice and salt. A dark greenish-blue liquid will condense, which contains nitrogen trioxide (N_2O_3). When the gas is conducted into ice-cold water, nitrous acid (HNO_2) is formed. When the greenish-blue liquid is evaporated, it produces a mixture of nitric oxide (NO) and nitric peroxide (N_2O_4), which probably contains traces of undissociated nitrous anhydride.

Nitrogen trioxide may also be made by mixing nitric oxide with oxygen, and cooling the mixture :—



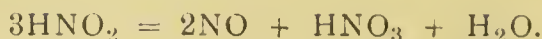
236. Nitrous acid and the nitrites. A solution of nitrogen trioxide in cold water reduces dilute solutions of chromates, and also of permanganates †, but it liberates iodine from iodides, and oxidizes ferrous salts.

A solution of nitrous acid gradually changes at ordinary tempera-

* The acid should have the density 1.25 (Thorpe).

† It will be remembered that several other oxidizing agents, e.g. ozone and hydrogen peroxide, exhibit a similar tendency to reduce other active oxidizers.

tures, producing nitric acid, which remains in solution, and nitric oxide :—



The nitrites, like the nitrates, are most of them decomposed by heat. They may be distinguished from nitrates easily owing to the fact that they emit red fumes when warmed with dilute mineral acids :—



If a solution of an iodide acidulated with dilute sulphuric acid be added to a nitrite, iodine is set free.

Nitrites are often present in water which has been contaminated by sewage. All those forms of organic matter which produce ammonia during putrefaction will generate nitrites, and then nitrates, in the presence of certain organisms. Hence the presence of nitrites in water may be accepted as an indication that its source is not properly protected from the entrance of sewage.

Nitrites may be formed by heating the nitrates of sodium or potassium, or by passing the fumes obtained by warming nitric acid with arsenious oxide or starch into a well-cooled solution of an alkali.

237. Nitric peroxide or nitrogen tetroxide (N_2O_4). The ruddy fumes which are produced when metals are dissolved in nitric acid, when liquid nitrous anhydride (N_2O_3) is evaporated, when nitric oxide is mixed with air, and when many nitrates are heated, probably owe their colour to the presence of this compound.

EXPERIMENT 176. To prepare nitric peroxide. Heat some well-dried nitrate of lead in a hard glass tube provided with a delivery tube, and connect the latter with a U tube immersed in a freezing mixture. Nitrogen peroxide will condense in the U tube, oxygen will escape, and lead oxide remain :—

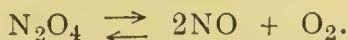


If the first portions of gas are condensed, they form a pale sherry-coloured liquid. The latter portions may be obtained as a crystalline solid, if they be cooled sufficiently.

EXPERIMENT 177. The properties of nitric peroxide. 1. Notice the colour of liquid nitric peroxide. It will grow deeper as the liquid becomes less cold after it is removed from the freezing mixture.

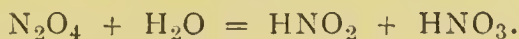
2. Pass a stream of nitric peroxide through a piece of combustion tube about 1 cm. in diameter. Notice its red-brown colour. Warm the middle part of the tube. The colour of the gas will become much

darker. Continue to heat the gas. You will presently observe that its colour fades till, at last, at about 600° , it becomes colourless owing to the destruction of the nitric peroxide :—

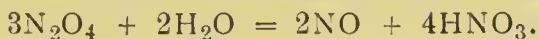


On recooling the heated gas the same phenomena will present themselves, but in the reverse order.

3. Pass a current of nitric peroxide into some water cooled by ice. It will dissolve completely, if it be pure, forming a solution which contains nitrous and nitric acids. [Try a test for the former.]



Pass some nitric peroxide into warm water. It will only partly dissolve, and nitric oxide will be formed and may be collected :—



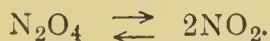
Question. If nitric peroxide be added to a cold alkaline solution, what will it form?

Nitric peroxide is a powerful oxidizer; it oxidizes mercury and sodium, liberates iodine from iodides, and reduces such substances as the permanganates. It supports the combustion of phosphorus, sulphur, and carbon if they be first well ignited.

238. The composition and formula of nitric peroxide.

As nitric peroxide attacks mercury we cannot analyse it by the method described in Experiment 180. But the fact that it can be made from nitrogen and oxygen, and its density (which is 22.9 at about 140°), lead us to conclude that its molecular formula at the latter temperature is NO_2 . This gas therefore affords us an example of a substance which does not obey the so-called law of even numbers*.

At low temperatures the density of nitric peroxide is much greater than at 140° . It therefore seems probable that when cold the gas consists largely of molecules having the formula N_2O_4 , but that they gradually dissociate under the influence of heat according to the following equation :—



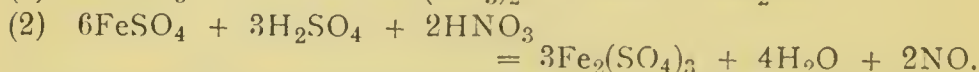
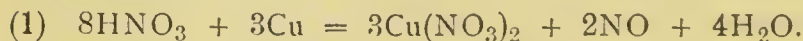
The molecular weight of liquid nitric peroxide has been found to be about 92 by the cryoscopic method (92). This corresponds to the formula N_2O_4 .

* That is, the sum of valencies of the atoms in its molecule is not an even number.

239. Nitric oxide (NO). EXPERIMENT 178. To prepare nitric oxide. 1. Place some copper in a flask provided with a delivery tube, and pour on it some nitric acid diluted with an equal weight of water.

2. Warm together a mixture of ferrous sulphate, nitric acid, sulphuric acid, and water. In each case a colourless gas will be evolved, which becomes ruddy in the air.

Equations:—

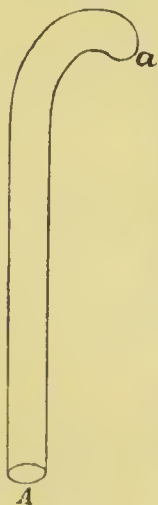


Nitric oxide is also produced, together with other gases, when other metals react with nitric acid, but it is usually prepared by one of the above reactions.

EXPERIMENT 179. Some properties of nitric oxide. 1. Mix a jar of oxygen with a jar of nitric oxide. Dense red fumes of nitric peroxide (N_2O_4) will be formed. This property distinguishes nitric oxide from all other gases, but nitric oxide and oxygen do not combine after they have been carefully dried.

2. Pass nitric oxide into a cold solution of a ferrous salt, and notice that a deep brown solution is formed. It is the forming of such a solution that causes the dark ring mentioned in Experiment 173.

3. Plunge a lighted taper into a jar of nitric oxide. It will be extinguished.



Plunge some phosphorus, well alight, into a jar of the gas. It will burn with increased brilliancy, as the temperature of the flame is sufficiently high to decompose the oxide.

Nitric oxide is more stable than the other oxides of nitrogen; it is not decomposed at a low red heat; it is not an anhydride, but attacks dry potash forming a nitrite and liberating nitrogen.

EXPERIMENT 180. To find the composition of nitric oxide. Collect a little nitric oxide over mercury in a 'thumb tube' (Fig. 91). Introduce a small piece of potassium into the gas, close the mouth *A* of the tube with the thumb, and jerk the potassium to *a*. Replace the tube in the mercury and heat the potassium; it will burn, forming oxide, as may be subsequently ascertained, and leaving nitrogen. Measure the nitrogen.

You will find that two volumes of nitric oxide yield one volume of nitrogen*.

Now the density of nitric oxide is 15 ($H = 1$), and the density of nitrogen 14.

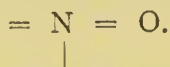
Therefore the relative weights of these volumes of nitric oxide and nitrogen are :—

$$\begin{array}{l} 2 \times 15 \text{ of nitric oxide.} \\ 1 \times 14 \text{ of nitrogen.} \end{array}$$

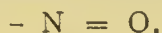
That is to say, 30 parts of nitric oxide contain 14 parts of nitrogen and 16 parts of oxygen. These proportions correspond to the formula NO .

As nitrogen is usually quinquivalent or trivalent in its compounds and oxygen divalent, the atoms forming a molecule of nitric oxide must have one or three of their valencies disengaged, as indicated by the following graphic formulae :—

Nitrogen quinquivalent.



Nitrogen trivalent.



Accordingly, at one time, chemists suspected that the true formula of nitric oxide might be N_2O_2 (see 238). But as the density of a gas having the formula N_2O_2 would be 30, this idea has now been abandoned.

240. Nitrous oxide, nitrogen monoxide or laughing gas (N_2O). The name laughing gas has been applied to this oxide of nitrogen owing to its curious power, discovered by Davy, of causing a temporary exhilaration when it is inhaled mixed with air or oxygen. If the gas be inhaled by itself, a brief sleep is induced, during which minor surgical operations may be performed, but if it be inhaled for too long the patient may be suffocated, in spite of the fact that nitrous oxide is a good supporter of combustion.

Nitrous oxide was discovered by Priestley in 1776. It is a frequent constituent of the gases evolved during the dissolution of metals in nitric acid, and, under some conditions, is said to be produced plentifully in such reactions, but it is usually prepared from ammonium nitrate (NH_4NO_3).

* You must not jump to the conclusion that one volume of oxygen also was present (see p. 196).

EXPERIMENT 181. To prepare nitrous oxide. Heat thirty or forty grams of ammonium nitrate in a flask provided with a delivery tube, taking care not to overheat the substance after the evolution of the gas has commenced. Collect the gas over hot water, or, after drying it, over quicksilver :—



EXPERIMENT 182. Some properties of nitrous oxide. 1. Plunge a burning candle into a jar of nitrous oxide. It will burn with added brilliancy.

Repeat the experiment using phosphorus and other combustible substances. If they are well alight when plunged into the gas they will burn as brilliantly as in oxygen, but if only feebly ignited they may be extinguished.

2. Place a jar of nitrous oxide mouth downwards in a basin of cold water. The gas will be rapidly dissolved by the water, for water at 0° dissolves more than its own volume of this gas.

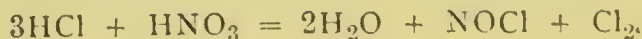
Nitrous oxide may be liquefied by a pressure of 50 atmospheres at 7.2°, and the liquid is prepared in this way on a considerable scale for the use of dentists. The liquid is lighter than water, boils at about - 90°, and if a fine jet of it be made to volatilize very quickly it freezes by its own evaporation.

241. The hyponitrites. It was once supposed that nitrous oxide might be the anhydride of an acid having the formula $(\text{HNO})_n$, just as nitrogen pentoxide (N_2O_5) is the anhydride of nitric acid (HNO_3).

If a solution of sodium nitrite in cold water be digested with sodium amalgam (415) till no more gas is evolved, then neutralized with acetic acid and mixed with solution of silver nitrate, it gives a precipitate of silver hyponitrite ($\text{Ag}_2\text{N}_2\text{O}_2$).

If this salt be suspended in water, and treated with dilute hydrochloric acid, the silver salt being kept in excess, it yields an acid solution which may contain hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$). This acid decomposes on standing.

242. Aqua regia. A mixture of nitric acid and hydrochloric acid dissolves gold and platinum, both of which resist the action of single acids; and it has been called in consequence 'aqua regia.' Aqua regia is supposed to owe its activity chiefly to chlorine, possibly to nascent chlorine, produced by the following reaction :—



243. Nitrosyl chloride (NOCl). If the gases given off by aqua regia be led into a U tube cooled by ice and salt, a dark-coloured liquid forms, which boils at about -8 . This is nitrosyl chloride; it is very stable, it slowly attacks many metals and combines with many of their chlorides. Water and alkalis decompose it:—



Nitrosyl chloride may also be made by warming dried salt (NaCl) with nitrosyl hydrogen sulphate* (NOHSO_4). The latter may be made by passing the mixture of chlorine and nitrosyl chloride, generated as above described, through oil of vitriol (see also p. 240).

244. Detecting nitrogen in its compounds. There is no single test by which nitrogen may be detected in all its compounds. The so-called 'ring test' (Expt. 173) may be employed to detect it in the state of nitrate or nitrite, and very minute quantities of nitrogen as nitrate or nitrite may be detected in an aqueous solution by adding a drop of a solution of diphenylamine sulphate, and then 1 c.c. of strong sulphuric acid to the solution, when a violet-blue coloured liquid is produced.

The following tests are also useful, but do not answer in the case of all compounds.

EXPERIMENT 183. 1. Burn some feathers or a scrap of cloth. The characteristic odour of the resulting substances is an indication that nitrogen is present.

2. Mix a little cheese intimately with excess of soda-lime, and heat the mixture gradually to redness in a hard-glass tube. Ammonia will be given off.

3. Heat a minute fragment of cheese, or of some other nitrogenous organic matter, strongly with a little potassium in a small tube. Dissolve the charred product in a little water, filter, add in succession a few drops of solutions of ferrous sulphate, ferric chloride, and soda, mix well and then add excess of dilute hydrochloric acid. The liquid will show a distinctly green colour, or yield flakes of a blue precipitate (Prussian blue).

* Tilden.

CHAPTER XVII

PHOSPHORUS AND ARSENIC

PHOSPHORUS (P_4): Atomic weight, 30.77.

245. WE have learnt already that phosphorus is a yellow, wax-like solid which readily burns in air, and also have met with a less inflammable substance called red phosphorus. The vapour density of phosphorus is about 62, at 1000° . Its molecular weight is therefore 124, and, as its atomic weight is 30.8, each molecule of phosphorus must contain four atoms of phosphorus.

Phosphorus in solution probably also has a molecule containing four atoms. [How was this ascertained?]

EXPERIMENT 184. **Some physical properties of phosphorus.**

1. Place a fragment of phosphorus under water in a test tube; immerse the test tube in a beaker of water, standing above a gas burner turned low; plunge the bulb of a thermometer into the water in the test tube, and watch till the phosphorus melts. This will occur at 44° . Now remove the flame and allow the water in the beaker to cool. The phosphorus will remain superfused till its temperature has fallen considerably, possibly till it reaches 32° ; but if a fragment of solid phosphorus be added at any stage the whole will quickly solidify.

2. If phosphorus be heated to about 280° in an atmosphere of carbon dioxide or nitrogen it will boil, but its boiling-point should *not* be determined by a young student.

3. Place a small piece of dry phosphorus in a tube *A* (Fig. 92), draw out its open end *B*, as in the figure, and connect it to an air-

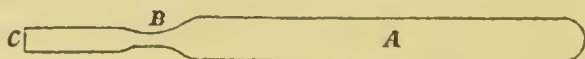


Fig. 92.

pump at *C*. Exhaust *A* as completely as possible, and seal it at *B*, whilst exhausted, before the blow-pipe. Place one end of the tube in water heated to about 40° . The phosphorus will presently sublime, condensing on the cooler parts of the tube in brilliant crystals.

EXPERIMENT 185. **Solvents for phosphorus.** **1.** Warm a fragment of phosphorus under some oil in a water bath. Then examine

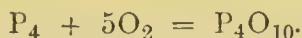
the oil in the dark. It will be found to be phosphorescent, owing to the presence of a little dissolved phosphorus.

2. Digest a fragment of phosphorus in a few drops of carbon disulphide, pour the solution on a sheet of bibulous paper, and allow it to evaporate. The incrustation of phosphorus left by the sulphide will be luminous in the dark, and, after exposure to the air for a few moments, will burst into flames.

Phosphorus, when pure, forms a transparent and almost colourless solid. When a stick of phosphorus is broken it shows evidence of possessing a crystalline structure, but it is soft enough to be cut with a knife at ordinary temperatures. When very cold it becomes hard and brittle.

EXPERIMENT 186. **Some chemical properties of phosphorus.**

1. Phosphorus, as we have already seen, burns freely in air and oxygen ; when excess of air is used, phosphoric anhydride (P_4O_{10}) is the chief product :—



2. Plunge a fragment of phosphorus, held in a deflagrating spoon, into a jar of chlorine. The phosphorus will at once ignite, forming chloride of phosphorus.

3. Warm a clean fragment of phosphorus in a dilute solution of chloride of gold. In a few minutes a layer of gold will be deposited upon the phosphorus, owing to the reducing power of the latter.

Phosphorus does not burn nor glow, even when heated to its boiling-point, in carefully dried oxygen.

EXPERIMENT 187. **To study the phosphorescence of phosphorus.**

1. Pass a slow current of air through a tube *B* (Fig. 93) containing

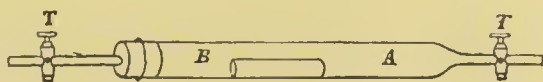


Fig. 93.

phosphorus in a dark room, and notice that the phosphorus is luminous. Then place a drop of turpentine on some bibulous paper at *B*, and continue the experiment. The phosphorus will no longer phosphoresce *. Remove the turpentine ; as soon as its vapour is expelled from *A* the phosphorus will again become luminous.

2. Pass a current of oxygen over the phosphorus in *A*. As soon as

* Ether and various essential oils may be used in place of turpentine.

the air is replaced by oxygen the phosphorus will again become non-luminous, unless the temperature be allowed to rise to 25° or 30° .

When the air in *A* has been replaced by oxygen, close *T*, connect the other end *T'* with an air-pump, and gradually exhaust the tube. Presently the phosphorus will again become phosphorescent. If a manometer be connected with the air-pump, it will be found that this occurs when about one-fifth of the oxygen remains.



Fig. 94.

3. Pass air over phosphorus and then over iodized starch paper. Iodide of starch will be produced. Smell the air as it passes from the phosphorus. The odour of ozone may be detected, for ozone and hydrogen peroxide are usually formed when phosphorus glows in air. Dr. Thorpe finds that most ozone is formed at 25° .

4. Place a stick of phosphorus in *A* (Fig. 94), place a little water in *B*, connect *C* with an aspirator, and draw air very slowly over the phosphorus. Fumes will descend to the water, which will soon acquire an acid reaction.

Evidently glowing phosphorus undergoes oxidation, for it forms an acidic oxide. This fact helps us to understand why phosphorus is apt to melt spontaneously, and afterwards to catch fire in air.

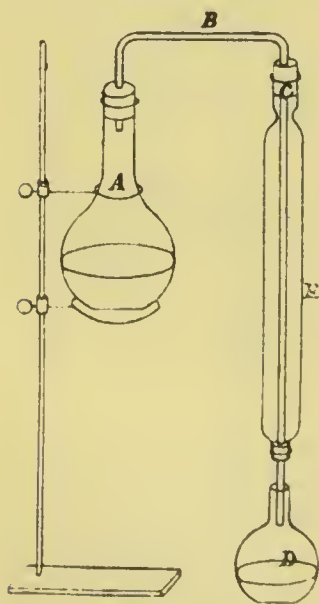


Fig. 95.

5. Having filled *A* (Fig. 93) with oxygen, and noticed that the phosphorus does not glow, pass a little ozonized oxygen over the phosphorus. It will at once glow*. This last experiment suggests that phosphorescence may be due to action between ozone and the vapour of phosphorus. In connection with this suggestion it must be remembered that turpentine, which destroys ozone (Expt. 101), kills the glow of phosphorus.

EXPERIMENT 188. To detect elemental phosphorus by its phosphorescence. Place a small fragment of phosphorus in a flask *A* (Fig. 95) together with some dilute sulphuric acid. Connect the flask with a condenser *E* and a flask *D*, and boil the contents of *A*. If the experiment be made in a dark room a phos-

* See Thorpe's *Chemistry*, i. 449.

phorescent glow will appear where the steam condenses in *B* or *E*, and, if enough phosphorus be present, some of it will collect in minute particles in *D*.

246. An allotropic form of phosphorus. EXPERIMENT 189. To prepare red or amorphous phosphorus*. Place a stick of phosphorus in a large bolt-head flask *A* provided with a cork carrying a short piece of tube *D* (Fig. 62), and apply heat till the phosphorus begins to boil. Remove the source of heat, and at once project a crystal or two of iodine into the phosphorus. The contents of the flask will quickly alter in appearance, owing to the formation of red phosphorus.

Red phosphorus is prepared on the large scale by heating common phosphorus out of contact with air for a considerable time. The product, which still contains much common phosphorus, is broken up, and boiled with caustic soda to destroy the latter (see phosphine, 251).

The density of red phosphorus varies from 2.1 to 2.2, that of white phosphorus being 1.84. Red phosphorus may be heated to a rather high temperature before it will melt or catch fire, and therefore it may be handled with safety. It is not luminous, and does not fume in damp air, but after long keeping is apt to become damp. If a little red phosphorus be shaken with carbon disulphide it will be found to be insoluble.

EXPERIMENT 190. To convert red phosphorus into white phosphorus. Heat two or three decigrams of red phosphorus strongly in a hard-glass tube. It will become luminous, and drops of a yellow liquid will condense on the cool upper parts of the tube†. Break the tube by letting it fall on an iron dish. The drops of liquid will ignite, giving off dense white fumes resembling those of burning phosphorus. These drops may be cooled under water, and identified by a more complete examination.

White phosphorus is exceedingly poisonous, but amorphous or red phosphorus is said to be inert.

The fact that these two substances are allotropic forms of the same element is established by the circumstance that either form may

* This experiment, and most of those in which phosphorus is used, should be made by the teacher.

† The red phosphorus of commerce often gives off phosphine (PH_3), and leaves a glassy residue when heated.

be converted into the other. Moreover, if equal weights of red and common phosphorus be burnt separately in excess of oxygen, equal weights of phosphoric oxide will be produced.

Red phosphorus is largely used in the composition placed on the boxes of safety matches. The heads of these matches are composed chiefly of antimony sulphide, chlorate of potassium, and glue; the composition on the boxes consists of red phosphorus with oxide of manganese, or sulphide of antimony, and glue. Common matches are tipped with a paste containing white phosphorus. The use of these latter is to be discouraged, as the fumes of the phosphorus are very injurious to the health of the 'dippers.'

If phosphorus be dissolved in molten lead, it separates, on cooling, in dark crystals, which are isomorphous with those of arsenic, antimony, and bismuth. Its density in this form is 2.34, and it may be separated from the lead by dissolving the latter in diluted nitric acid.

247. Phosphorus an element. When phosphorus enters into combination with oxygen, it produces one or more oxides, but any one of these oxides can be converted into the others by increasing or reducing the proportion of phosphorus. In no case does it behave like marsh gas when it is oxidized, or when it combines with other elements (see 122); and we know no class of compounds resembling phosphorus. Therefore it is considered to be an element.

248. The sources and manufacture of phosphorus. Phosphorus exists, as phosphate, in many of the older rocks, and is found in the soil formed by their disintegration. From the soil it is absorbed by the roots of plants, and thence passes into the bodies of animals. It is present, in greater or less quantity, in most animal tissues, and earthy phosphates constitute the chief part of the mineral components of bone. The student may easily extract calcium phosphate from fragments of bone by digesting them in solution of hydrochloric acid. After a few hours a stiff gelatinous mass (osseine) will remain, and if the liquid be decanted and neutralized with ammonia the calcium phosphate will be precipitated. The residue is used for making glue.

Bones, apatite (phosphate of calcium), redonda phosphate (aluminium phosphate), and coprolites are the chief sources of phosphorus.

Phosphorus was discovered, in 1669, by Brand. To obtain it, bones *

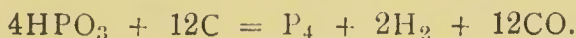
* Mineral phosphates, such as apatite, are often substituted for bone-ash.

are either burnt, or extracted with superheated water to remove the ossein, which is sent to the glue-makers. The residue is ground to a powder and digested with sulphuric acid, which liberates phosphoric acid:—



The acid solution is decanted, or strained, from the insoluble sulphate of calcium, concentrated, and mixed intimately with charcoal. The mixture is then heated to whiteness in clay retorts *A* (Fig. 96), which are connected with iron pipes *B*, dipping into warm water in *D*.

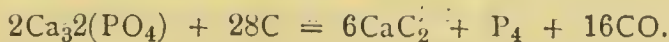
The heat first dehydrates the phosphoric acid, forming metaphosphoric acid (HPO_3), and the latter is reduced by the carbon at higher temperatures:—



The crude phosphorus from *D* is melted under water, strained through bags of wash-leather, and run into tubes, where it is allowed to solidify. It may be further purified by shaking it, when melted, with a mixture of potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and strong sulphuric acid.

Pure phosphorus is *almost* colourless, and translucent; but it gradually becomes covered by an opaque crust, which seems to consist of amorphous phosphorus, especially if it be not protected from light.

Since the introduction of the electric furnace it has been found possible to decompose calcium phosphate directly by the action of carbon. The following reaction is said to occur:—



249. The waste of phosphates by civilized communities.

Under the conditions of modern life, a great part of the phosphates and other soluble matters removed from the soil by plants and afterwards consumed by men are not returned to the soil, as they

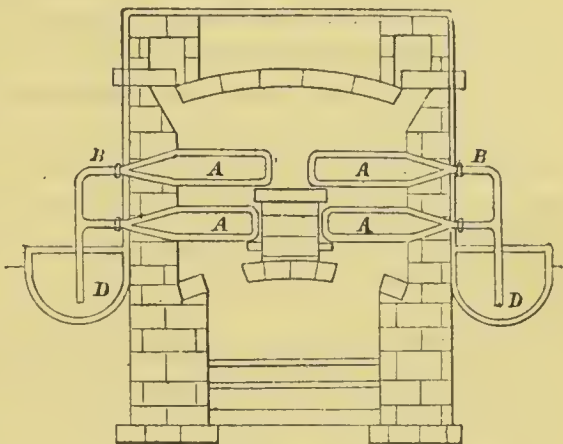


Fig. 96.

should be, but are cast into the sea, and thus, as far as one is able to judge, permanently lost *. Of course fresh supplies of phosphates are continuously liberated by the 'weathering' of the rocks; but this process proceeds slowly, and probably does not counterbalance the exhausting effect of a long series of crops, when these are largely consumed away from their place of production. It is true that a certain amount of the matter carried from the land is returned to the soil in the form of farmyard manure, and that a certain amount of the calcium phosphate of bones is sent back to the farmer as 'soluble phosphate' or in some other form. But, after allowing for this, the annual loss must be very great, and farmers endeavour to make up for it by putting on the land various imported manures, such as guano (the excrement of birds), and preparations made from coprolites (the fossilized excrements of former inhabitants of the earth), and redonda phosphate.

250. The atomic weight of phosphorus. To determine the combining weight of phosphorus. Obtain a small thin glass bulb, blown on the end of a piece of fine glass tube. Weigh this. Introduce a little pure trichloride of phosphorus into it by warming the bulb and plunging the tip of the tube into the liquid. Close the bulb by melting off part of its neck, and reweigh it together with the bit of tube removed.

Introduce the bulb and its contents into a well stoppered bottle, together with 60 or 70 c.c. of distilled water, a few drops of pure nitric acid, and a weighed quantity of silver nitrate †. Close the bottle securely, agitate it violently in order to break the bulb and liberate its contents, and continue the agitation for eight or ten minutes. All the chlorine will then be precipitated as chloride of silver.

1. Prepare a solution of hydrochloric acid of known strength by diluting some strong acid (see 116).

2. Filter the liquid from the precipitated silver chloride obtained as above described; wash the chloride repeatedly with water, and add the washings to the filtrate; make up the volume of the filtrate and washings to 200, 300, or 400 c.c. as may be convenient.

3. Add the standard solution of hydrochloric acid to an aliquot part of the solution of silver from a burette, till the last drop gives

* Sir William Crookes estimates the annual loss from this source at £16,000,000. Such a sum would purchase sixteen ironclads.

† This should weigh about six times as much as the chloride of phosphorus.

no precipitate of silver chloride *, and note how much standard acid is employed.

From the amount of hydrochloric acid required, calculate how much silver was left unacted upon by the chloride of phosphorus.

Subtract this from the weight of silver taken to find how much has been converted into chloride by the chloride of phosphorus. 107.1 parts of silver require 35.2 of chlorine to convert it into chloride.

From the amount of silver converted into chloride by the chloride of phosphorus, and from the above data, calculate the amount of chlorine in the chloride of phosphorus taken, and the amount of phosphorus which was combined with one equivalent proportion of chlorine.

If a similar experiment were made with the solid chloride of phosphorus, it would be found that whilst an equivalent weight of chlorine is combined with 10.27 parts of phosphorus in trichloride of phosphorus, the same quantity of chlorine is combined with no more than 6.16 parts of phosphorus in the solid chloride.

Phosphorus enters into the composition of several volatile compounds, and it has been found that the quantity of the element present in a molecular proportion of such a compound is never less than 30.8 (10.27×3 , or 6.16×5). Moreover when the amount is greater than this, as it is in the oxides, it is a multiple of 30.8.

251. Phosphorus and hydrogen. Phosphine, phosphur-

etted hydrogen,
trihydrogen phosphide (PH_3).

EXPERIMENT 191. To prepare trihydrogen phosphide. 1. Heat some fragments of phosphorus in a flask *A* (Fig. 97), filled to the level *C* with solution of soda, or with baryta water, after expelling the air from *A* and *E* by passing a current of

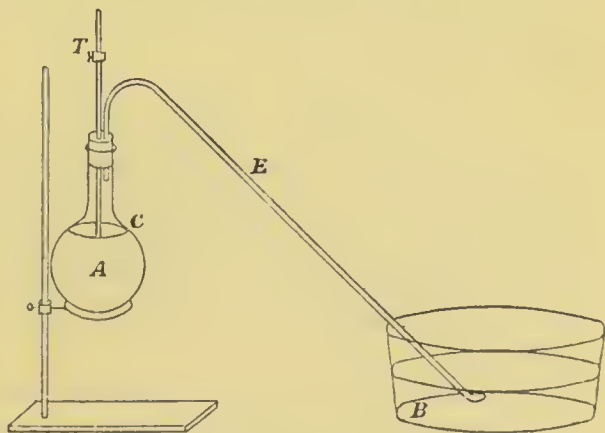


Fig. 97.

coal gas through *T*. A gas will be given off which bursts into flames

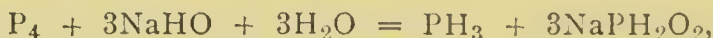
* If the flask be frequently and violently agitated, the precipitate will settle at a certain stage almost completely, and it will not be very difficult to hit the desired point afterwards.

as it escapes from the water in *B*. This gas consists largely of phosphine.

By cooling the spontaneously inflammable gas, we can obtain a less combustible gas and a highly combustible liquid. The latter corresponds in composition to the formula P_2H_4 , and it is doubtless the cause of the singular qualities of phosphuretted hydrogen prepared by the action of phosphorus on alkalis.

When the inflammable liquid is exposed to the sun it is resolved into gaseous phosphine, and a solid which is supposed to be represented by the formula P_4H_2 .

The production of phosphine by the action of phosphorus with an alkali is usually represented as follows:—



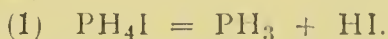
but as the process proceeds hydrogen is produced, together with sodium phosphate, by the action of the alkali on the sodium hypophosphite ($NaPH_2O_2$).

Phosphine may also be made:—2. By throwing calcium phosphide on water. When made in this way it is accompanied by the liquid phosphide.

3. By adding phosphorous chloride (PCl_3) to water, and strongly heating the resulting phosphorous acid (H_3PO_3):—



4. By cautiously adding (1) water, or (2) an alkali, to phosphonium iodide (PH_4I):—



Some properties of phosphine. The phosphine prepared from phosphorous acid, or from phosphonium iodide, is a colourless gas, which ignites spontaneously in air at 100° . It possesses an odour resembling that of decaying fish. It requires a very low temperature to liquefy it, -90° , and if further cooled it yields a crystalline solid which melts at -134° .

When phosphine is collected over mercury, and submitted to the electric discharge, it decomposes like ammonia (Expt. 164), 2 volumes of phosphine yielding 3 of hydrogen. The vapour density of a sample of phosphine, which was probably not quite pure, was 17.2 ($H = 1$). Hence 34.4 parts of phosphine contain 3 parts of hydrogen and 31.4 of phosphorus; or, more correctly, since the respective atoms of these elements weigh 1 and 30.8, 3 parts of hydrogen with 30.8 parts of phosphorus.

Unlike ammonia, phosphine is insoluble in water. Consequently, if a fragment of phosphonium iodide be thrown on water, the phosphine may be seen to escape, and may be recognized by its smell. It is not alkaline, but combines with one or two of the acids.

252. Phosphonium. If red litmus be held in phosphine it will remain unaffected. On the other hand, when phosphine is mixed with one of the hydrogen halides, or passed into well-cooled oil of vitriol, it yields salts analogous to those of ammonium. Thus we may get :—

Phosphonium iodide	PH_3, HI	or	$(\text{PH}_4)\text{I}$
„ bromide	PH_3, HBr	„	$(\text{PH}_4)\text{Br}$
„ chloride	PH_3, HCl	„	$(\text{PH}_4)\text{Cl}$
„ sulphate	$(\text{PH}_3)_2, \text{H}_2\text{SO}_4$	„	$(\text{PH}_4)_2\text{SO}_4$

These compounds are only stable at low temperatures and in the absence of water, and phosphonium iodide alone can be preserved in dry air at ordinary temperatures.

Phosphonium iodide may be prepared by adding iodine to a solution of phosphorus in carbon disulphide, evaporating the solvent, dropping water slowly upon the residue in the retort, and heating the product in a current of carbon dioxide; the phosphonium iodide then sublimes.

253. Phosphorous chloride or phosphorus trichloride.

EXPERIMENT 192. To prepare phosphorous chloride (PCl_3).

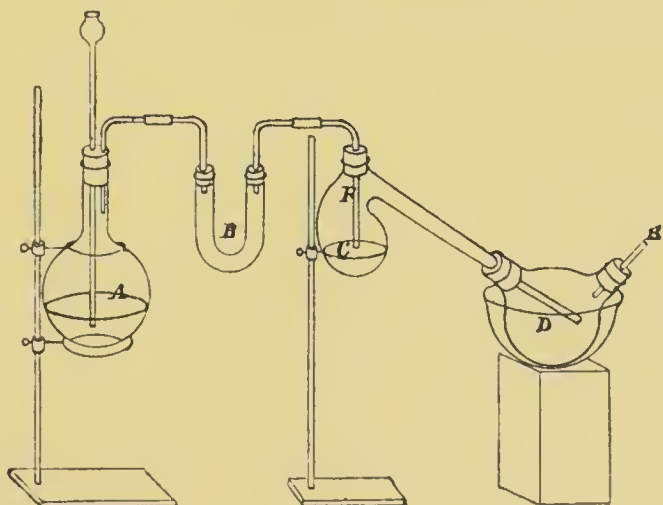
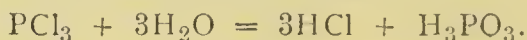


Fig. 98.

Generate chlorine in *A* (Fig. 98). Place pumice-stone soaked with sulphuric acid in *B*, and some dry phosphorus in *C*. Let the

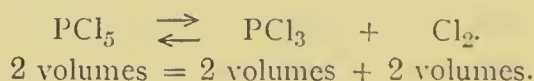
chlorine pass slowly over the phosphorus by *F*, and conduct the excess, if any, from *E* to a flue. The phosphorus and chlorine will produce a liquid which may be condensed in the receiver *D* if it be kept cool. This liquid is phosphorus trichloride.

Phosphorus trichloride boils at 76° . It absorbs oxygen, when hot, forming the oxychloride POCl_3 ; unites with chlorine, forming the pentachloride PCl_5 ; and acts rather vigorously with water, yielding phosphorous acid (H_3PO_3) and hydrochloric acid:—

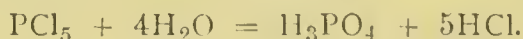


Phosphorous chloride does not undergo dissociation when volatilized.

254. Phosphorus pentachloride or phosphoric chloride (PCl_5). EXPERIMENT 193. To prepare phosphoric chloride or phosphorus pentachloride. Pass a current of well-dried chlorine into a small quantity of phosphorus trichloride. A pale yellow mass of the pentachloride will be produced. This substance fuses at 148° under pressure. The density of its vapour is abnormal, that is to say, it decreases with rise of temperature, and at 300° is about half as great as the value suggested by theory, but as free chlorine may be detected in the vapour by diffusion, it is now understood that the compound dissociates (see 198):—

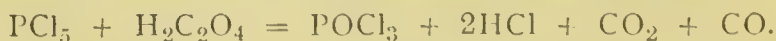


Phosphoric chloride fumes in damp air, and dissolves in water, forming phosphoric acid (H_3PO_4) and hydrochloric acid:—



When only a small quantity of water is used, phosphorus oxychloride (POCl_3) is formed.

255. Phosphorus oxychloride or phosphoryl trichloride (POCl_3). This is a colourless liquid which boils at 107° , and reacts with water, producing phosphoric and hydrochloric acids. [Work out the equation.] It may be made by the action of water on the pentachloride; by heating together, under proper pressure and in proper proportions, phosphorus pentoxide and phosphorus pentachloride; or by treating dry oxalic acid with phosphorus pentachloride:—



The action of the above compounds on substances containing hydroxyl has already been discussed.

256. Other compounds of phosphorus with halogens.

Phosphorus forms a trifluoride (PF_3) and a pentafluoride (PF_5). The latter is a colourless gas. It is prepared by treating arsenic trifluoride (AsF_3) with phosphorus pentachloride (PCl_5). The existence of this gas, which is stable at high temperatures, is of considerable interest, because it shows that phosphorus can exist as a quinquivalent element in combination with a halogen in gaseous molecules.

EXPERIMENT 194. **To obtain iodide of phosphorus.** Dissolve about 2 decigrams of phosphorus in a little carbon disulphide, add about ten times as much iodine, then evaporate the solution. Orange-red crystals will be deposited together with dark-red prisms. The former (P_2I_4) melt at 110° , the latter (PI_3) at 55° . Both are decomposed by water.

Other compounds, such as the tribromide (PBr_3), the pentabromide (PBr_5), which readily dissociates like the corresponding chloride, phosphoryl bromide (POBr_3), phosphoryl fluoride (POF_3), thiophosphoryl chloride (PSCl_3), and thiophosphoryl bromide, are also known.

THE OXIDES AND OXYACIDS OF PHOSPHORUS.

Three oxides of phosphorus are definitely known, viz. phosphoric oxide (P_4O_{10}), phosphorous oxide (P_4O_6), phosphorus tetroxide (P_2O_4).

257. Phosphoric anhydride, phosphoric oxide (P_4O_{10}).

If phosphorus be burnt under a bell jar, or in a small chamber, a white solid can be collected. This consists mainly of phosphoric oxide, though it will reduce mercuric chloride (HgCl_2) to mercurous chloride (Hg_2Cl_2), owing to the presence of small quantities of the lower oxides of phosphorus. These may be removed by passing a mixture of the vapour of phosphoric oxide and oxygen over platinized asbestos heated to redness. When pure it has no reducing power.

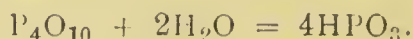
EXPERIMENT 195. **Some properties of phosphoric oxide.**

1. Expose about a gram of phosphoric oxide to the air. It will quickly become gummy, and finally will form a syrupy acid solution. Dissolve a little phosphoric oxide in water, boil half the solution for half an hour with a little acid or alkali, neutralize each part with soda, and add a drop or two of solution of silver nitrate.

The solution which has been boiled will give a yellow precipitate of silver phosphate (Ag_3PO_4).

The unboiled portion will give no yellow precipitate with silver

nitrate, because it will not contain phosphoric acid, but metaphosphoric acid (HPO_3) :—

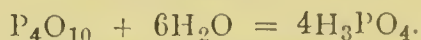


Phosphoric oxide is extensively used as a dehydrating agent (see nitrogen pentoxide, 234) on account of the readiness with which it combines with water. There would appear to be two distinct forms of this oxide: one is amorphous, the other crystalline. The latter is easily prepared by subliming the commercial oxide. It was long given the formula P_2O_5 , but Dr. W. A. Tilden and Mr. R. E. Barnett have recently found its vapour density to be 142 ($\text{H} = 1$). Therefore its formula should be written P_4O_{10} .

Phosphoric oxide yields the following series of acids by combining with water :—

Orthophosphoric acid		H_3PO_4 .
Pyrophosphoric acid		$\text{H}_4\text{P}_2\text{O}_7$.
Metaphosphoric acid		HPO_3 .

258. Orthophosphoric acid. EXPERIMENT 196. Preparation and properties of orthophosphoric acid. We have already learnt that phosphoric acid is produced when phosphoric oxide is boiled with water containing a little acid or alkali (Expt. 195) :—



Also that makers of phosphorus obtain the same acid by digesting bone ash with sulphuric acid (248).

On the small scale it may be made conveniently by the direct oxidation of red phosphorus.

1. Place two or three grams of red phosphorus, moistened with water, in a capacious flask, cover it with strong nitric acid, and warm the contents of the flask very cautiously, removing the source of heat as soon as the action begins. When most of the phosphorus has disappeared, boil off the excess of nitric acid, dissolve the residue in water, and boil the solution.

Phosphoric acid as thus prepared forms a sour solution which is very acid to litmus, and neutralizes alkalis. If concentrated *in vacuo*, till its density is 1.8 ($\text{H}_2\text{O} = 1$), it will crystallize on the addition of a fragment of the solid acid. Its simplest formula is H_3PO_4 , and, for reasons which follow, this expression is also accepted for its molecular formula.

Experiments with phosphoric acid. 1. Neutralize a little of your

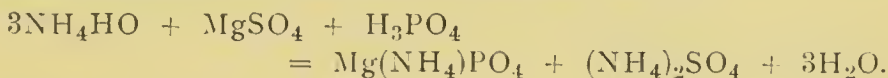
phosphoric acid with ammonia, and add some solution of silver nitrate. A yellow precipitate of silver phosphate (Ag_3PO_4) will fall.

2. Heat a few crystals of phosphoric acid to about 215° in a tube immersed in heated oil for some time, dissolve a little of the product in *cold* water, and neutralize the solution. It will now give a white precipitate of silver *pyrophosphate* with solution of silver nitrate.

3. Heat part of the pyrophosphoric acid, or some phosphoric acid, to redness; on cooling, a colourless, glassy solid will remain, which will become damp if exposed to the air. This is metaphosphoric acid (HPO_3), commonly called 'glacial phosphoric acid.'

4. Warm a little solution of phosphoric acid with some solution of mercuric chloride, or with silver nitrate in the presence of excess of ammonia; in neither case will any evidence of reduction be observed (see Expt. 203, 2).

5. Add solution of ammonia to some phosphoric acid, then a solution containing magnesium sulphate, and ammonium chloride. A precipitate of ammonium and magnesium phosphate will fall:—



The exact composition of the precipitate is expressed by the formula $\text{Mg}(\text{NH}_4)\text{PO}_4, 6\text{H}_2\text{O}$.

The basicity of phosphoric acid. The simplest formula for phosphoric acid which is consistent with its composition and with the atomic weights of its constituents is H_3PO_4^* . Therefore its molecular formula must be H_3PO_4 , or some multiple of this.

By suitable treatment with soda (see 114), we can replace its hydrogen in three stages, producing a series of salts which stand to one another and to the acid in the relations expressed by the following formulæ:—

H_3PO_4		Phosphoric acid
NaH_2PO_4		Monosodic phosphate
Na_2HPO_4		Disodic phosphate
Na_3PO_4		Trisodic phosphate.

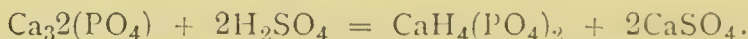
We therefore conclude that the acid is tribasic.

259. Salts of orthophosphoric acid. Phosphates. Only the orthophosphates of the alkali metals are soluble in water, the other

* 98 parts of the acid contain one atomic proportion of phosphorus, i. e. 31 parts. Therefore 98 is the smallest value we can adopt for its molecular weight. 98 parts of the acid contain also 3 parts of hydrogen and 64 parts of oxygen.

phosphates are insoluble. Therefore most orthophosphates may be prepared by precipitation. A phosphate may be recognized by some of the tests given above (258), and by the production of a yellow precipitate when a very dilute solution of the salt in nitric acid is added to excess of a solution of molybdate of ammonium.

We have already learnt that calcium phosphate is our chief source of phosphorus. This salt is largely used as a manure, for which purpose it is converted into calcium tetrahydrogen phosphate ($\text{CaH}_4\text{2PO}_4$), which is known in commerce as 'superphosphate of lime' or soluble phosphate, by treating bones or coprolites with oil of vitriol, in the proportions indicated below :—



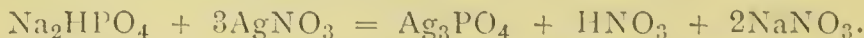
EXPERIMENT 197. To prepare sodium phosphate. Digest one molecular proportion of 'bone earth,' in powder, with three molecular proportions of sulphuric acid, add water, boil, filter, and neutralize the solution of phosphoric acid thus prepared with sodium carbonate, or hydroxide. Filter, and evaporate the solution till crystals form on cooling. Recrystallize the salt from a solution in hot distilled water, and preserve the crystals.

EXPERIMENT 198. To learn if the salt made by neutralizing phosphoric acid with soda is trisodic phosphate. The results of our previous experiments would lead us to suppose that the salt last made must have the formula Na_3PO_4 , for we have found usually that when an acid is neutralized by a base, the basic hydrogen of the acid is replaced completely by the metal of the base.

Add silver nitrate to a solution of the above salt till the precipitate of silver phosphate, Ag_3PO_4 , ceases to fall, filter the solution, and test it with litmus. You will find it contains free acid. Now, trisodic phosphate (Na_3PO_4) and silver nitrate (AgNO_3) would not interact in such a way as to yield free acid and triargentic phosphate, but as follows :—



On the other hand, a phosphate containing hydrogen, such as Na_2HPO_4 , might produce free acid with silver nitrate. Thus:—



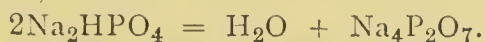
Hence the salt we have made cannot have the formula Na_3PO_4 , but it may be disodic phosphate (Na_2HPO_4), or monosodic phosphate (NaHPO_4).

A study of the relative quantities of acid and alkali required to produce our salt (see 114) would show us that it is the disodic

phosphate (Na_2HPO_4)*. Moreover, as we shall presently see, by adding acid to it in proper proportions, we can convert it into the monosodic phosphate (NaH_2PO_4), and by adding more alkali we can convert it into a third salt, which must be the trisodic phosphate (Na_3PO_4). Finally, its behaviour when strongly heated confirms the opinion that the product of neutralizing phosphoric acid with soda corresponds to the formula Na_2HPO_4 .

Disodium hydrogen phosphate is commonly known as phosphate of soda. It occurs in colourless rhombic prisms, which correspond to the formula $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

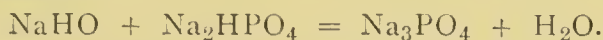
When strongly heated it loses water, forming sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) (see 260):—



It gives a yellow precipitate with silver nitrate in neutral solutions, and generally exhibits the reactions of phosphoric acid (258).

EXPERIMENT 199. To make trisodium phosphate (Na_3PO_4 , $12\text{H}_2\text{O}$).

Take a weighed quantity of sodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) and add the amount of soda (NaHO) required to convert it into trisodium phosphate:—

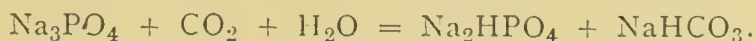


Evaporate the solution till it crystallizes. The resulting crystals, if perfect, will be six-sided prisms which melt at 77° .

Heat a fragment of trisodic phosphate strongly, dissolve the residue in cold water, and add solution of nitrate of silver. White pyrophosphate of silver will not be obtained in this case, but the ordinary yellow triargentic phosphate (Ag_3PO_4), for trisodic phosphate is not altered by heat.

Examine the behaviour of a solution of trisodic phosphate with red litmus, and with some very dilute acid. It will turn the former blue, and neutralize the latter like an alkali.

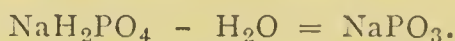
Expose some crystals of the salt, or a solution of them, in water to the air, or to carbon dioxide, for some hours. Examine the action of dilute acid upon them. A carbonate will be found to be present:—



* Owing to its being a little difficult to obtain pure phosphoric acid, the student cannot very well study the subject from this latter standpoint for himself. He may, however, obtain some solution of phosphoric acid of known strength, neutralize it with standard soda, and calculate the composition of the salt formed.

EXPERIMENT 200. To prepare and study the properties of sodium dihydrogen phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$). Add phosphoric acid to a solution of sodium phosphate till the liquid no longer gives a precipitate when a drop of it is mixed with solution of barium chloride. Concentrate the solution as much as possible and cool it strongly. Prismatic crystals of monosodic phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) will form. These will be found to be acid to litmus, to neutralize alkalis, and to be very soluble.

Heat some of the crystals strongly, treat the product, when cold, with cold water and test it with nitrate of silver *. You will find that a metaphosphate has been formed (see 261):—

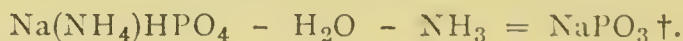


EXPERIMENT 201. To make and study microcosmic salt ($\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$). Make a solution of six parts of sodium phosphate in two parts of hot water, add one part of ammonium chloride, remove the common salt (NaCl), which separates, by filtering, and concentrate the filtrate. Crystals of microcosmic salt will be deposited.

1. Heat minute fragments of various salts, such as calcium carbonate and phosphate, in small beads prepared by fusing this salt on a loop of platinum wire before the blow-pipe. You will find they are all dissolved.

Make a similar experiment with silica or a silicate. The silica will remain floating in the melted salt. This affords us a useful test for silica.

2. Heat a little microcosmic salt in a platinum basin till it fuses. The residue will consist of sodium metaphosphate:—



260. Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$). A crystalline mass containing this acid may be produced by exposing phosphoric oxide to air in a loosely closed vessel. It is also produced when orthophosphoric acid is heated to 215° (258); and it may be made by heating disodium hydrogen phosphate (Na_2HPO_4), decomposing a solution of the sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) thus produced with lead nitrate, washing the precipitated lead pyrophosphate ($\text{Pb}_2\text{P}_2\text{O}_7$),

* No precipitate will be obtained, as NaPO_3 , when thus made, is almost insoluble in water.

† If it be overheated a heavy insoluble residue may be produced.

decomposing it, when suspended in water, with hydrogen sulphide and concentrating *in vacuo* the solution thus prepared.

Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) is readily converted into metaphosphoric acid (HPO_3) by heat. Its solution is gradually reconverted into orthophosphoric acid if it be boiled with water.

It may be distinguished, as we have seen, by its white insoluble silver salt (258), and by its gradual transformation into phosphoric acid when in aqueous solution. It is tetrabasic.

261. Metaphosphoric acid (HPO_3 or $\text{H}_2\text{P}_2\text{O}_6$). This acid may be obtained, as a glassy solid, by heating orthophosphoric acid to redness; also by heating microcosmic salt, converting the sodium metaphosphate thus produced into the insoluble lead salt, and treating the latter, suspended in water, with hydrogen sulphide. When phosphoric anhydride (P_4O_{10}) is dissolved in cold water, the solution contains metaphosphoric acid.

Tilden and Barnett have determined the vapour density of this acid, and they give it the formula $\text{H}_2\text{P}_2\text{O}_6$. Its salts are apparently rather complex, and occur in several polymeric forms. Thus there are monometaphosphates ($\text{M}'\text{PO}_3$), dimetaphosphates ($\text{M}'_2\text{P}_2\text{O}_6$), trimetaphosphates ($\text{M}'_3\text{P}_3\text{O}_9$). The monometaphosphates of potassium and sodium (KPO_3 and NaPO_3) are made by heating the corresponding dihydrogen phosphates ($\text{M}'\text{H}_2\text{PO}_4$) or microcosmic salt ($\text{NaNH}_4\text{HPO}_4$) to redness, till the residue is almost insoluble.

Solutions of soluble metaphosphates are converted into orthophosphates by long-continued boiling. They give white precipitates with nitrate of silver and coagulate albumen in the presence of acetic acid.

Hypophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$) is said to occur among the products of the slow oxydation of phosphorus in damp air. It is tetrabasic, and without much reducing power, but potassium permanganate converts it into phosphoric acid. Several of its salts are known.

262. Phosphorous oxide, phosphorous anhydride (P_4O_6). When phosphorus is burnt in a limited supply of air, a white powder is produced, which possesses considerable power as a reducing agent. This probably contains some phosphorous oxide, but Thorpe has recently prepared this oxide of phosphorus in a pure state, for the first time, in the following manner:—

Sticks of phosphorus were placed in a glass tube *A* (Fig. 99), which is connected with a brass tube *B*, placed inside a jacket *C*, like that of

a Liebig's condenser. *C* was filled with water and provided with a thermometer *D*. The end of *B* nearest *E* was plugged with glass

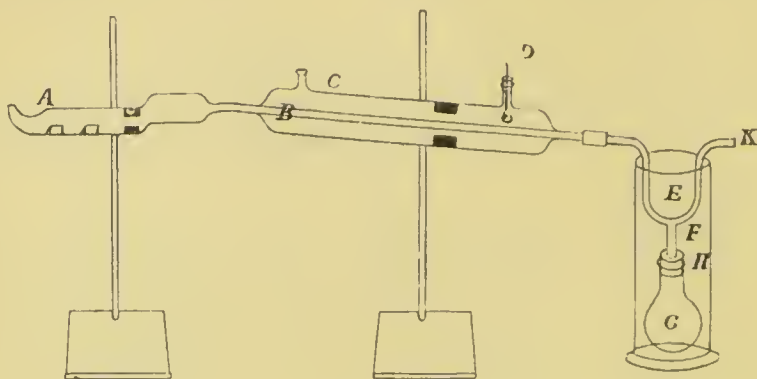
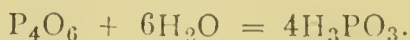


Fig. 99.

wool for a length of about 6 cm., and connected to a U tube *E*, which, in its turn, was joined by *F* to a receiver *G*. *E*, *F*, and *G* were surrounded by a freezing mixture in the cylinder *H*. A current of air was drawn through the apparatus by means of a pump connected with *K*, and the phosphorus was heated. When the phosphorus had slowly burnt for about a quarter of an hour, *B* and *C* were heated to 50°, afterwards to 60°. Phosphorous oxide condensed and fell into *G*, any phosphoric oxide that might be formed being stopped by the plug of glass wool, and retained in *C*. The product of the above operation was a colourless substance, which melted at 22.5° and boiled at 173.1°. Its vapour density and the freezing-point of its solution point to the molecular weight, 220. Hence its formula is P_4O_6 .

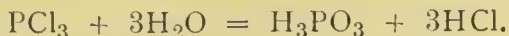
Phosphorous oxide dissolves slowly in cold water, forming phosphorous acid:—



With water at 100°, however, it behaves differently, giving phosphuretted hydrogen in considerable quantity, together with a solution of phosphoric acid, in which there is suspended a red solid, resembling amorphous phosphorus. When it is dissolved in cold alkali a phosphite is produced. When this substance is exposed to air or oxygen, at ordinary temperatures, it is gradually oxidized to phosphoric oxide (P_4O_{10}), and it burns readily in oxygen below 60° with a very brilliant flame.

263. Phosphorous acid (H_3PO_3). EXPERIMENT 202. To

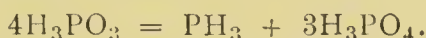
prepare phosphorous acid. 1. Add a few drops of phosphorous chloride (PCl_3) gradually to some well-cooled water :—



If the product be carefully concentrated at a low temperature, it will yield crystals of phosphorous acid.

2. Draw air mixed with the vapour of phosphorus trichloride through a little water until a mass of crystals is obtained.

EXPERIMENT 203. Some properties of phosphorous acid. 1. Evaporate a few drops of a solution of phosphorous acid over a Bunsen burner. Water will be given off, and a somewhat syrupy liquid will remain, which will presently appear to catch fire. This is due to the fact that phosphorous acid is converted into phosphoric acid and phosphuretted hydrogen by heat :—



2. Warm some solution of phosphorous acid with a few drops of solution of mercuric chloride (HgCl_2). A precipitate of mercurous chloride (Hg_2Cl_2) will fall. This acid will also reduce ammoniacal silver nitrate.

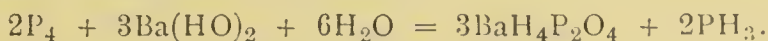
3. Neutralize a little phosphorous acid with sodium hydroxide, and add to it some solution of calcium or barium chloride. A precipitate of calcium or barium phosphite will form.

As most of the phosphites, except those of the alkali metals, are insoluble in water, they may be prepared by precipitation. The soluble phosphites are said to be fairly permanent in air, but they are converted into phosphates by oxidizing agents.

The basicity of phosphorous acid. The phosphites of sodium and potassium that have been definitely isolated correspond to the formulæ $\text{M}'_2\text{HPO}_3$ and $\text{M}'\text{H}_2\text{PO}_3$, but as all the hydrogen of the acid can be replaced by the compound radicle ethyl (C_2H_5), we may perhaps

adopt the formula $\left. \begin{array}{c} \text{HO} \\ \text{HO} \\ \text{HO} \end{array} \right\} \text{P}$ or $(\text{HO})_3\text{P}$ for the acid.

264. Hypophosphorous acid (H_3PO_2). When phosphorus is boiled with a solution of potash, soda, or baryta, phosphuretted hydrogen is evolved (251), and a salt of this acid is formed. The reaction is usually written as follows :—



If an equivalent quantity of dilute sulphuric acid be added to a

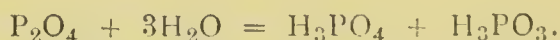
solution of the barium salt, hypophosphorous acid will be liberated. It may be separated from the insoluble barium sulphate by filtering.

Hypophosphorous acid is strongly acid to litmus. It can be obtained as a crystalline mass by concentrating its solution *in vacuo*. It is a powerful reducer, and is gradually oxidized to phosphorous and phosphoric acids, when exposed to the air.

When heated it yields phosphoric acid and phosphine. It may be distinguished from phosphoric and phosphorous acids by the solubility of its calcium and barium salts, by its power of reducing solutions of mercuric chloride, and by the fact that, when warmed with a slightly acid solution of copper sulphate, it yields a red precipitate of *copper hydride* (Cu_2H_2).

265. Phosphorus tetroxide (P_2O_4). When the product of burning phosphorus in a slow stream of air is heated to 290° in an exhausted tube it gives a white crystalline sublimate of phosphorus tetroxide.

This oxide forms colourless, highly lustrous crystals, which volatilize at 180° . It dissolves in water, yielding phosphorous and phosphoric acids :—



(Compare nitrogen tetroxide, 237.)

266. Phosphorus and sulphur. Phosphorus combines with sulphur when heated with it. The following sulphides are said to have been prepared :—

Phosphorus monosulphide	. .	$\text{P}_4\text{S} (?)$
„ sesquisulphide	. .	P_4S_3
Phosphorous sulphide	. . .	P_4S_6
Phosphoric sulphide	. . .	P_2S_5 or $\text{P}_4\text{S}_{10} (?)$.

These sulphides dissolve in solutions of the alkalis, forming compounds in which sulphur may be considered to replace the oxygen of the phosphates and phosphites.

ARSENIC (As_4) : Atomic weight, 74.4.

267. This element is sometimes found native, but it occurs chiefly as a constituent of various minerals. *Realgar*, or *ruby sulphur* (As_2S_2), and *orpiment* (*auri pigmentum*) (As_2S_3), are well-known sources of arsenic, and oxidized arsenic is occasionally met with in water. It is most familiar in the form of its oxide, white arsenic

(As_4O_6), which is obtained by roasting various minerals, such as the arsenides of iron, nickel, cobalt, and arsenical pyrites, in air, and condensing the arsenic in suitable chambers or flues.

As a rule, experiments in which arsenic is used should be made by the teacher, or under his direct supervision, as it is highly poisonous.

EXPERIMENT 204. To prepare elemental arsenic. Mix a very little white arsenic (As_4O_6) with excess of carbon, or with some cyanide of potassium, and heat them in a hard-glass tube. A compact lustrous layer of arsenic will condense on the cooler parts of the tube.

Arsenic crystals are isomorphous with those of the allied elements antimony and phosphorus. The compact lustrous form of arsenic, which condenses on hot surfaces, is permanent in air, but the element may also be obtained as a steel-grey powder, and in this state it is oxidized at ordinary temperatures. At ordinary atmospheric pressure it volatilizes without melting.

Its vapour density is 149.8 ($H = 1$). Hence its molecular weight is 300 (see 91). And, therefore, since its atomic weight is 75, we give it the formula As_4 . At temperatures greatly above 1500° its density is lower, and its molecules may then be diatomic. Its vapour has an odour resembling that of garlic.

268. Arsenic and hydrogen. Arsine. **EXPERIMENT 205.** The preparation and properties of arsenic trihydride (AsH_3).
1. Place zinc and hydrochloric acid in a small hydrogen generator, and, when the air is expelled, add a drop or two of a solution of arsenic in hydrochloric acid. Signs of increased action will be observed, and the hydrogen will acquire an unpleasant odour, which is caused by the presence of arsine (AsH_3). Ignite the escaping gas at a jet, and notice the peculiar lavender-coloured flame with which it burns. Hold a cold porcelain dish in the flame. A black stain of elemental arsenic will form upon it.

Pass some of the gas through a dilute solution of silver nitrate. A precipitate of silver will fall :—



Filter the liquid, and pour some very dilute solution of ammonia on its surface. A yellow precipitate of silver arsenite will form where the two liquids meet.

If the gas be passed through a hot tube it deposits arsenic. The above experiments are often employed as tests for arsenic.

Arsine is best prepared by dissolving zinc arsenide in dilute acid, but it should by no means be made by a student, on account of its poisonous character.

A solid hydride of arsenic (As_4H_2) is also known. It is a brown combustible powder.

269. Arsenious oxide. EXPERIMENT 206. To crystallize and study the properties of arsenious oxide (As_2O_3). Heat a minute fragment of white arsenic cautiously in a small tube of hard glass. Brilliant but minute crystals will condense on the cool upper parts of the tube. Examine these with a lens. You will observe minute octahedra among them.

Break off the closed end of the tube used for Experiment 204, and heat the deposit of arsenic. It will disappear, and crystals similar to those just examined will form on the cooler parts of the tube.

Freshly sublimed arsenic is often met with in dense, transparent, glassy masses, which are destitute of crystalline structure. If these be exposed to moist air they gradually become opaque, owing to the forming of minute crystals, and ultimately assume the appearance of a dense enamel. There is also a prismatic form of arsenious oxide.

The crystalline forms of arsenic are converted into an inodorous gas, without previous fusion at 220° ; and the density of its vapour corresponds to the formula As_4O_6 . The vitreous form melts before volatilizing.

Arsenious oxide is *exceedingly* poisonous. It is used as an anti-septic, and in medicine.

Reactions. 1. Warm a little white arsenic with some water. It will dissolve, but not readily, giving a faintly acid solution, which may be supposed to contain *arsenious acid* (H_3AsO_3).

2. Add a little solution of silver nitrate to some of the solution, and neutralize it with dilute ammonia; a yellow precipitate of *silver arsenite* (Ag_3AsO_3) will form.

3. Add a little solution of copper sulphate to the solution of arsenic, and neutralize it carefully with ammonia. A beautiful green precipitate of copper arsenite, or Scheele's green (CuHAsO_3), will fall. This substance was at one time much employed for colouring wall-papers, but its use has been discontinued owing to its highly poisonous qualities.

The Arsenites. Alkaline arsenites may be obtained by dissolving arsenious oxide in solutions of potash or soda. These are alkaline in

reaction, and very easily decomposed by weak acids, arsenious oxide being deposited in crystals. The sodium salt is used by calico printers.

270. Arsenic oxide. Arsenic anhydride (As_2O_3 or As_4O_{10}). Arsenic oxide is decomposed when strongly heated. Consequently its vapour density is unknown; but since the formula of phosphoric oxide is P_4O_{10} , it seems likely that the formula of the corresponding oxide of arsenic may be As_4O_{10} . Like phosphorus pentoxide it forms an acid; arsenic acid.

EXPERIMENT 207. To prepare arsenic oxide and study its properties. 1. Dissolve a gram or so of white arsenic in a little hydrochloric acid, add some nitric acid, and boil the mixture so long as red fumes are evolved. Evaporate the product, and heat the solid residue to *low* redness in a fume closet, taking care to avoid inhaling the fumes. The residue will consist of arsenic acid.

2. Heat a little arsenic oxide in an ignition tube. Notice that it does not sublime below a red heat, but that it gives a sublimate of arsenious oxide, together with oxygen, at higher temperatures:—



3. Place a little arsenic oxide in water. It will dissolve, after some delay, giving an acid solution which gradually deposits crystals of arsenic acid ($2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$) when concentrated.

These crystals yield *orthoarsenic acid* (H_3AsO_4) when heated to 100° , and this acid is converted into *pyroarsenic acid* ($\text{H}_4\text{As}_2\text{O}_7$) at 180° , and into metarsenic acid (HAsO_3) at 200° . At a *low* red heat it yields the anhydride (As_4O_{10}). All these are reconverted into arsenic acid when they are redissolved.

4. Neutralize some solution of arsenic acid with ammonia, then add a few drops of a solution of silver nitrate. A chocolate-coloured precipitate of silver arsenate (Ag_3AsO_4) will fall.

5. To another portion of the acid add solutions containing ammonia and ammonium chloride, and then some magnesium sulphate. A white precipitate of magnesium and ammonium arsenate ($\text{Mg}(\text{NH}_4)\text{AsO}_4 \cdot 6\text{H}_2\text{O}$) will form (compare $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$, Expt. 196, 5).

Arsenic acid is tribasic [write the formulæ of the possible arsenates of sodium], and many arsenates are isomorphous (339) with the compounding phosphates. Sodium arsenate is used by dyers and calico printers, and in the making of dyes from the constituents of coal tar.

Arsenic acid is said to be less poisonous than arsenious acid.

If hydrogen sulphide be passed into solutions of arsenious oxide and arsenic oxide separately, it will be found that the former readily gives a precipitate of arsenious sulphide (As_2S_3), but that the latter gives no precipitate unless it has been heated with strong hydrochloric acid.

271. Sulphides of arsenic. *Realgar* or *ruby sulphur* (As_2S_2) is found native, and is a constituent of *white fire*.

Arsenious sulphide (As_2S_3 or As_4S_6) also occurs native, as *orpiment*; it may be made by passing hydrogen sulphide through a solution of arsenious oxide. It is a yellow, volatile solid, which dissolves in strong solutions of alkalis, and also in solutions of alkaline sulphides, forming salts called *thioarsenites*. The thioarsenites of the alkali metals are soluble; acids decompose them, liberating arsenious sulphide.

Arsenic sulphide (As_2S_5 or As_4S_{10}) is also a yellow solid, which is soluble in solutions of the sulphides of the alkali metals. Three thioarsenates of potassium, viz. KAsS_3 , $\text{K}_4\text{As}_2\text{S}_7$, and K_3AsS_4 , have been described; they correspond to the metarsenate, pyroarsenate, and orthoarsenate of the same metal. Like the thioarsenites, these compounds are decomposed by acids, arsenic sulphide being one of the products of the change.

272. Arsenic and the halogens. Arsenic readily burns in chlorine, bromine, and iodine, and two fluorides (AsF_3 and AsF_5) are known. The latter occurs in the compound $2(\text{KF} \cdot \text{AsF}_5) \cdot \text{H}_2\text{O}$.

Arsenious chloride (AsCl_3). Arsenic burns in chlorine, forming this chloride, which may also be obtained by distilling arsenious oxide with strong hydrochloric acid. It is a colourless, oily liquid, which boils at about 130° . In contact with a small quantity of water it is said to form an oxychloride ($\text{AsClO} \cdot \text{H}_2\text{O}$); with excess of water it yields arsenious acid and hydrogen chloride.

Arsenious bromide (AsBr_3) is a colourless, crystalline solid, which reacts with water like the corresponding chloride. The pentachloride and pentabromide of arsenic are unknown.

Arsenic forms a di-iodide (AsI_2), a tri-iodide (AsI_3), and probably also a pentiodide (AsI_5). All these are crystalline substances.

273. Detecting arsenic. Arsenic may be detected as hydride in the manner described in 268, or by one or more of the reactions mentioned in 269–70. When it is mixed with beer, gruel, or other substances containing organic matter, the suspected material may be

heated with one-tenth of its weight of pure oil of vitriol, or with some strong hydrochloric acid and chlorate of potassium, and filtered. The arsenic may then be precipitated by means of hydrogen sulphide. Arsenic may also be extracted from the solution by boiling in it some fragments of pure copper foil. The arsenic then collects on the surface of the foil, and if this be dried, cut into strips, and heated in an ignition tube, the arsenic will sublime, yielding characteristic crystals of the oxide on the cooler parts of the tube. These may be dissolved, and the solution may be submitted to the various tests mentioned in the previous pages.

274. A comparison of the members of Group V. Nitrogen, phosphorus, arsenic, &c. If you now compare what you have learnt about nitrogen, phosphorus, and arsenic, with what you previously learnt about sulphur, selenion, and tellurium, and about the halogens, you will find that though the first three elements are non-metals, they differ in many respects from the members of the other groups. Thus whilst nitrogen, phosphorus, and arsenic are trivalent in their typical compounds with hydrogen, and whilst their hydrides are either basic, like ammonia, or neutral, the members of the other two groups are respectively divalent and univalent in their hydrides, and these are for the most part acidic in character. Again, whilst acids corresponding to a heptoxide of the type R_2O_7 are formed by some of the halogens, and whilst acids corresponding to trioxides (RO_3) are formed by the members of the sulphur group *, the highest oxides formed by members of the nitrogen group belong to the type R_2O_5 or R_4O_{10} .

On the other hand, a close examination of the members of the nitrogen group reveals certain marked differences among the properties of its members. Thus the molecules of nitrogen are diatomic (N_2), but those of phosphorus and arsenic contain four atoms. Phosphorus and arsenic readily combine with oxygen and with the halogens, but nitrogen does not combine directly with the latter, and does not readily unite with oxygen. Nitrogen forms no acids of the types H_3RO_4 , H_3RO_3 (see phosphoric and phosphorous acids, 258, 263), but only forms acids of the *meta* type, HNO_3 and HNO_2 (see metaphosphoric acid), and this element does not, as far as we know, exhibit allotropy like phosphorus and arsenic.

Thus the resemblance between phosphorus and arsenic, which, together with antimony and bismuth, make up the known odd series

* Sulphur also forms a heptoxide (S_2O_7).

members of Group V, is greater than the resemblance between these elements and nitrogen. Both form hydrides, which are less stable and less basic than ammonia. Both combine directly with the halogens, and their halides are more stable than those formed by nitrogen. Arsenic and phosphorus burn readily in oxygen, and are oxidized by nitric acid, but nitrogen does not readily form oxides by direct combination. Phosphorus is a non-conductor, but arsenic conducts somewhat better, and resembles a metal in appearance. Neither phosphorus, arsenic, nor nitrogen replace the hydrogen of acids.

Antimony and bismuth will be discussed more fully at a subsequent stage, but it may be pointed out here that these elements, which have greater atomic weights and higher densities than phosphorus and arsenic, are harder and more metallic in appearance than the latter. They are fairly good conductors, and may be obtained by reducing their oxides with carbon at high temperatures. Both burn in air. Both form oxides of the type M_2O_3 . Both unite with chlorine, bromine, and iodine. Both are oxidized by nitric acid, and bismuth forms a nitrate ($Bi(NO_3)_3$). The oxides of antimony, though slightly basic to acids, are acidic to strong bases, forming compounds called antimonates, and the oxides of bismuth, though more basic, are not quite without acidic functions. When the chlorides of these elements are acted on by water, they form oxychlorides ($SbOCl$ and $BiOCl$). A hydride of antimony can be obtained by a similar process to that by which arsine is prepared, but no hydride of bismuth has been met with.

The other members of Group V are of less importance to a beginner, but vanadium will be briefly discussed in the later pages of this book.

CHAPTER XVIII

CARBON AND SILICON

CARBON (C): Atomic weight, 11.91.

275. THIS element exists, almost pure, in the form of diamond, and also as graphite or plumbago, both of which are crystalline. It is also familiar, but in a much less pure state, in the forms of charcoal, coke, soot, jet, and coal, which are amorphous.

The compounds of carbon are very widely spread, very plentiful, and of immense importance. Carbonate of calcium (limestone) exists in great quantity in the form of chalk, marble, oolite and coral, and in many sea-shells and in pearls. Magnesium carbonate is plentiful as magnesite, and in dolomite, a double carbonate of calcium and magnesium, and other carbonates are met with in nature. Carbon is present in the tissues of plants and animals, and it is an important constituent of the mineral oils (paraffin) and of wax.

The *diamond* is found in several localities, e.g. in India, Borneo, South Africa, and Brazil. It is crystalline, transparent, and may be obtained quite colourless.

We do not know how diamonds have been formed in nature, but diamond has been made by heating iron containing carbon in the electric furnace, and then cooling it rapidly by plunging it in a bath of molten lead. The iron when dissolved leaves a residue which contains adamantine carbon.

Diamonds are not only used for decorative purposes, but, owing to their great hardness, the less perfect specimens are valuable for cutting, grinding, and polishing other hard substances.

In crystalline form, diamonds are cubical, or octahedral, or exhibit some figure belonging to the cubical system (339, I).

The octahedral crystals are often bounded by curved faces as in Fig. 100 *b*; they are then especially suitable for cutting glass*. The density of diamond varies from 3.3 to 3.5; and it is a non-conductor.

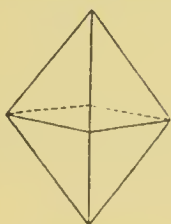


Fig. 100 *a*.

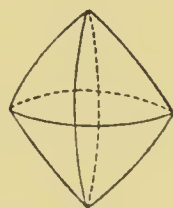


Fig. 100 *b*.

Diamonds are infusible, but burn if strongly heated in oxygen, yielding carbon dioxide. They are converted into a kind of coke if heated to a very high temperature, away from air. Carbonado and bort are varieties of diamond used for polishing. The former contains a little lime and iron.

Graphite. EXPERIMENT 208. To extract graphite from cast

* See *Laboratory Arts*, by R. Threlfall, p. 78.

iron. Place some iron filings in excess of dilute hydrochloric acid. When all action is over, collect the residue on a filter, wash it well with water, and dry it. You will now have a specimen of more or less impure graphite.

Native graphite, which is found in various localities, usually contains mineral matter together with traces of oxygen and hydrogen. When crystalline, it occurs in hexagonal plates or short prisms*. It is obtained chiefly from Ceylon, the United States, and Germany. Very good graphite was at one time found at Borrowdale, in Cumberland.

The density of graphite is 2.2. It conducts electricity; its ready friability renders it a good lubricant, and it is used for polishing gunpowder. It appears to be formed when carbon is exposed to molten iron in the blast furnace (489), and sometimes separates from molten iron, as it cools, in bright scales called *k'ish*. Its well-known power of marking paper has led to its extensive use in 'black-lead' pencils. Native graphite occurs as 'foliated graphite' and as 'amorphous graphite.' The latter is most suitable for pencils, but it is apt to contain gritty particles of silicious matter. These may be removed by digesting it in hydrofluoric acid.

If graphite mixed with nitric acid and chlorate of potassium be exposed to the sun, a crystalline substance called graphitic acid ($C_{11}H_4O_5$) is formed. Another acid called mellitic acid ($C_6(COOH)_6$) may also be prepared by oxidizing graphite. It is doubtful whether these substances would be yielded by *pure* graphitic carbon.

Amorphous carbon is commonly one of the products of the incomplete combustion of organic substances, and is familiar in the form of soot. It may be prepared by igniting resin or camphor, out of contact with air. When made in this way it is termed *lampblack*. An impure form, *charcoal*, is made in large quantities by the 'destructive distillation' of wood.

EXPERIMENT 209. To obtain charcoal from wood. Destructive distillation. Pack a tube (Fig. 101) with fragments of wood, place it over a Ramsay, or a Fletcher burner *D*, after corking the end, connect it with a U tube or flask provided with a jet, and gradually heat the wood to redness. You will obtain:—

1. Combustible vapours which may be ignited at the jet. These contain, amongst other things, hydrogen and marsh gas.

* Carbon is therefore dimorphous.

2. A tarry distillate. This is a useful preservative from which creosote is prepared.

3. A watery distillate, which is acid to litmus, and from which wood spirit and acetic acid are prepared.

4. A residue of impure carbon or charcoal in the tube.

In countries where wood is plentiful charcoal is prepared from the less valuable parts of trees, by igniting them in heaps covered with earth, so that the supply of air is very limited. Under these conditions the volatile products are lost, but a great part of the carbon remains. In countries where wood is more valuable the other products are carefully secured.

Coke is an impure form of carbon which remains when coal is strongly heated.

Animal charcoal or bone black is made by distilling bones or other animal matter. It consists very largely of mineral matter; that made from bones may contain only about 10 per cent. of carbon. Animal charcoal possesses remarkable powers of absorbing organic substances from solutions, and is used for refining brown sugar and for similar purposes.

EXPERIMENT 210. To decolourize a liquid by means of bone charcoal. Digest a little powdered bone charcoal with diluted claret, or weak solution of indigo, then filter the mixture. The filtrate will be colourless.

EXPERIMENT 211. Some properties of carbon. 1. Throw fragments of charcoal and graphite into a basin of water. The former will float, the latter will sink. But amorphous carbon is honeycombed with pores. These must contain air. Let us endeavour to get rid of this air.

2. Powder some charcoal finely, that the air may escape, and throw it on water. It will now sink.

3. Immerse a piece of charcoal, tied to a stone, in a beaker containing water; place the beaker under the receiver of an air-pump and exhaust the receiver. Bubbles of air will be seen to escape from the charcoal owing to its expansion under reduced pressure. Detach the stone, and again put the charcoal under water; if it has been sufficiently freed from air it will now sink.

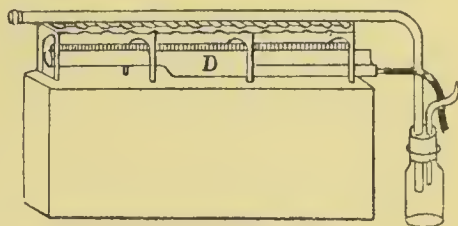


Fig. 101.

The density of amorphous carbon is 1.5 to 1.8, that of graphite being about 2.2 and that of pure or nearly pure diamond 3.5.

4. Prepare a few pieces of charcoal by carbonizing fragments of cocoa-nut shell, under sand, in a crucible. Introduce pieces of the freshly made charcoal into tubes containing ammonia, hydrochloric acid gas, and sulphur dioxide, collected over mercury. The mercury will rise, for the charcoal absorbs these gases. Carbon dioxide, oxygen, nitrogen and hydrogen are also absorbed by carbon, but not to an equal extent. Freshly made charcoal sometimes ignites spontaneously when exposed to air, owing, it would seem, to the rapid absorption of oxygen.

5. Place a fragment of flesh at the bottom of a deep cylinder, and fill up the cylinder with roughly broken charcoal. No offensive odour will arise from the flesh until a considerable time has elapsed. This may be due to the carbon absorbing the offensive gases, and perhaps partly to the oxidizing of the latter by oxygen previously condensed in the charcoal.

It has been found that a cubic centimetre of freshly made cocoa-nut charcoal will absorb 171 c.c. of ammonia, 86 c.c. of nitric oxide, and 68 c.c. of carbon dioxide.

Wood charcoal is much less absorbent. One cubic centimetre of it takes up 9 c.c. of oxygen, 6 c.c. of nitrogen, and 1 c.c. of hydrogen.

Amorphous carbon does not conduct electricity.

EXPERIMENT 212. To obtain pure carbon. Heat small but equal portions of wood charcoal, and bone charcoal, to redness in uncovered crucibles. In each case an ash will remain, that from bone charcoal being by far the more considerable. Then prepare a little charcoal by charring some refined sugar in a covered crucible, and burn some of it as before. The sugar charcoal will leave very little ash, for refined sugar contains but little mineral matter.

But even sugar charcoal does not consist of pure carbon, for it yields a little water when burnt, owing to the presence of hydrogen. This hydrogen, together with some oxygen, may be removed by igniting the charcoal strongly in a current of chlorine.

Carbon an element. When purified carbon is burnt with excess of oxygen it forms a colourless incombustible acid gas and yields no other product. It does not, for example, yield two products as marsh gas does. It must therefore be regarded as an elementary substance. This conclusion is confirmed by the fact that carbon has not been recomposed by heat, electricity, &c.

276. The identity of the three forms of carbon and the combining weight of carbon. The combustion of the diamond was first effected, at the focus of a burning glass, in 1694 by members of the Academia del Cimento. About a century later the French chemists discovered that it produces carbon dioxide when burnt, and it was thereafter classified with carbon.

Graphite was confused with sulphide of molybdenum, and supposed to contain lead, till Scheele, in 1779, showed that it yields carbon dioxide when it is oxidized with nitric acid. The fact that diamond, graphite, and amorphous carbon are allotropic forms of one element has since been conclusively established by such experiments as that which is described below.

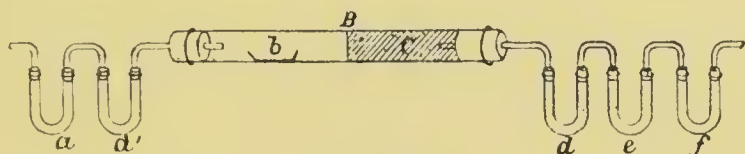


Fig. 102.

Some diamond, pure amorphous carbon, or pure graphite is weighed in a platinum dish *b* (Fig. 102), which is introduced into a combustion tube *B*, containing a column of copper oxide at *C*. *B* is placed in a furnace, the weighed absorption tubes *d*, *e* and *f* are placed in position, and the copper oxide is heated to redness; then the rest of the tube is heated, and a slow stream of oxygen purified by the action of solution of potash in *a* and dried by means of sulphuric acid in *a'* is passed over the hot carbon. The carbon burns, any monoxide that may be formed is converted into dioxide at *C*, the dioxide is absorbed by solution of potash in the tube *d*, and the water-vapour carried from the potash in *d* is absorbed by strong sulphuric acid in *e*. The tube *f* contains sulphuric acid to prevent moisture from the air reaching *e*. When the carbon is consumed a current of air is drawn through the apparatus to sweep all the carbon dioxide into *d*. *b* is then reweighed, and so are *d* and *e*. From the data thus obtained we can find the weight of carbon burnt, and the weight of carbon dioxide formed.

When this experiment is made with diamond, graphite, and carbon, respectively, it is found that 1 part of each yields 3.67 parts of carbon dioxide, and no other product, if the substances are pure. Hence these three substances must all consist of the same element.

277. The equivalent weight of carbon. 1 part of carbon combines with 2.67 parts of oxygen. Therefore 2.98 parts of carbon would combine with 7.95 of oxygen. But 7.95 parts of oxygen are equivalent to 1 part of hydrogen. Therefore the equivalent weight of carbon is 2.98, or approximately 3.

278. Some chemical properties of carbon. We have already learnt that carbon burns readily in air, forming two oxides, viz. carbon dioxide (CO_2), an acid gas, and carbon monoxide (CO), a neutral combustible gas. Also that it forms two sulphides, which are analogous to the oxides in composition and in some of their properties (207). Further we have seen that it does not combine directly with the halogens, nor with nitrogen. Carbon is our most important fuel, and also a most valuable reducing agent. Thus phosphorus and arsenic are liberated from their oxides by its aid (248), and it is very extensively used in reducing the metallic oxides, as we shall learn from the following pages.

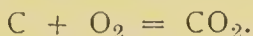
Though carbon is not distinguished for its readiness to enter into direct combination with the other elements, it is truly remarkable for the number and variety of the compounds into which it enters, and it plays a rôle of the greatest importance in the life-processes of both animals and vegetables. Up to the latter part of the eighteenth century our knowledge of the chemistry of the carbon compounds advanced slowly. Many carbonaceous substances were known and made use of in medicine and in the arts, but their composition and their relations to one another were, for the most part, still undetermined. But after Lavoisier had placed chemistry on a new foundation, chemists began to examine organic substances * from a purely scientific point of view, with the result, first, that many new and interesting substances were discovered by Scheele and others ; and, secondly, that Liebig, after teaching us how to analyse such compounds, revolutionized this branch of chemistry by introducing, in conjunction with Wöhler, the idea of 'compound radicles †.' From that time an army of workers has laboured at organic chemistry, and to-day the known compounds of carbon probably greatly exceed in number the compounds of all the other elements put together. But this is not all. Up to 1828 it was almost an axiom that certain substances, such as sugar and starch, could only be produced within the bodies of plants or animals under the influence

* 'The chemistry of the carbon compounds has been called 'organic chemistry.'

† See 105.

of a so-called 'vital force.' This idea was shattered by Wöhler, who produced one of the most characteristic products of animal life, viz. urea (289), from ammonium cyanate (NH_4CNO), by the action of heat. From that day the preparing of substances of this class in the laboratory has been one of the chief objects of chemical research.

279. Carbon dioxide. EXPERIMENT 213. The method of making carbon dioxide. 1. Pass a moderately rapid stream of oxygen over charcoal heated to redness in a hard glass tube (Fig. 130), and examine the action of the gas produced on lime-water and on litmus. It will be found to resemble carbon dioxide. The following is the reaction by which it is formed:—



2. Place lumps of marble, or some other form of limestone, in a bottle like that used for making hydrogen, or in a 'Kipp' (Fig. 77), and add some diluted nitric or hydrochloric acid. A gas will be given off freely which is heavier than air, and which exhibits the qualities of carbon dioxide:—



Try similar experiments with magnesite or any other carbonate that may be available.

3. Heat bicarbonate of sodium, or of potassium, in a hard-glass tube provided with a delivery tube. Carbon dioxide and water will be given off:—



4. Repeat the last experiment using magnesite (MgCO_3). At high temperatures this also will give off carbon dioxide. On the manufacturing scale a great deal of carbon dioxide is generated by heating magnesite (MgCO_3) and limestone (CaCO_3):—



5. All compounds of carbon, when burnt in excess of air, generate carbon dioxide. It is produced by the decay of organic matter, and escapes from volcanoes.

The liquid carbon dioxide supplied for chemical and other work is largely collected from the fermenting vats in breweries (see 298).

Carbon dioxide is one of the constituents of atmospheric air (see 68).

280. The properties of carbon dioxide. *Physical properties*

of carbon dioxide. Carbon dioxide, as we have seen, is a colourless, odourless gas. It is more soluble in water than oxygen, hydrogen, or nitrogen, and it is used in making aerated waters. Its density (60) is about 22 ($H = 1$), and therefore it can be collected by downward displacement of air. Under a pressure of 36 atmospheres, at 0° , it condenses to a colourless limpid liquid, which is lighter than water, more expansible, when heated, than air, and which mixes in all proportions with ether, alcohol, and carbon disulphide. Its critical temperature is $+31.5^{\circ}$, its critical pressure 73 atmospheres. When liquid carbon dioxide is allowed to escape from a fine jet, part of it evaporates, and thereby lowers the temperature of the remainder to its freezing-point, so that it falls as a snow-like solid. Solid carbon dioxide does not evaporate very quickly, and it may be handled safely, provided that it is not pressed closely against the skin. Faraday employed a mixture of solid carbon dioxide and ether as a freezing-mixture in his experiments on the liquefaction of gases.

EXPERIMENT 214. The chemical properties of carbon dioxide. 1. Plunge a lighted candle into a jar of carbon dioxide. It will be extinguished as in nitrogen. Repeat the experiment, using sulphur and phosphorus. You will obtain similar results.

This quality renders carbon dioxide very harmful to animal life, for just as it does not support combustion, so it will not support life. Hence places in which this gas abounds, such as brewers' vats, old wells or cellars containing decaying organic matter, or caves in which it is emitted from the earth, are dangerous unless they have recently been well ventilated. Carbon dioxide is one of the constituents of the deadly *after-damp* of coal mines, which so often destroys those who have escaped the direct effects of explosions.

The air of confined spaces does not become unwholesome solely through the presence of carbon dioxide. If an unventilated place be crowded with people, or if a fire burn in such a place, the air not only gains carbon dioxide, but also receives, in the first case, other unwholesome exhalations and, in the latter, the products of destructive distillation or of imperfect combustion. In both cases the available supply of oxygen is gradually diminished. But the presence of a great excess of carbon dioxide in the air is in itself dangerous, for air which contains 10 per cent. of this gas will produce insensibility and ultimately death. As a candle will not burn in air containing more than this proportion of carbon dioxide, a taper may be used to test the fitness of air for inspiration; but although a man cannot live

in air in which a candle will not burn, it does not follow that one may safely remain for long in an atmosphere in which a candle will burn, for as little as 2 per cent. of carbon dioxide may produce serious effects if the full proportion of oxygen be not present in the air. Air containing above 0.06 per cent. of carbon dioxide may be regarded as impure. A simple test of the quality of air is the following :—Place 20 c.c. of well-made lime-water in a bottle capable of holding 400 c.c., fill the rest of the bottle with the air to be tested, close the bottle and shake the air and lime-water together violently. If the lime-water does not become turbid, the air does not contain much more than 0.06 per cent. of carbon dioxide. This test is based on the fact that *saturated* lime-water does not become turbid until one eighty-fourth of its volume of carbon dioxide has been absorbed, because calcium carbonate is not absolutely insoluble in water.

2. Plunge a strip of burning magnesium into a jar of carbon dioxide. The metal will continue to burn, and after the experiment black particles of carbon mingled with a white solid, which is alkaline to damp litmus, will be found in the jar. The white solid is oxide of magnesium (MgO) :—



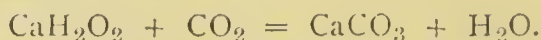
Carbon dioxide is also reduced by carbon at a red heat (see carbon monoxide, 282).

3. Collect some carbon dioxide in narrow tubes over mercury. Add, by means of a pipette, some solution of potash or soda, or some lime-water, to the contents of one tube, and some damp solid potash to those of a second tube. Notice that the gas is freely absorbed in each case.

Pass a stream of carbon dioxide through some water, and afterwards examine the action of the water upon dilute soda and on blue litmus. It will not neutralize the former, but will give a wine-red colour to the latter. Possibly an acid is formed.

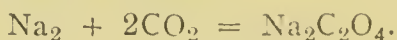
4. Pass a stream of carbon dioxide through about 250 c.c. of lime-water ; collect the precipitate and examine the action of acids upon it. It will effervesce, giving off carbon dioxide. Therefore it is a carbonate. Moisten a particle of the precipitate with solution of hydrogen chloride, and hold it in a Bunsen flame on a platinum wire. It will give an orange-red colour to the flame. On p. 414 you will find that this is one of the characteristics of calcium. Therefore the

precipitate must be calcium carbonate. The following equation explains its formation :—

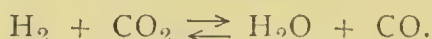


5. Repeat the last experiment, using 50 c.c. of lime-water, but continue to pass the carbon dioxide through the lime-water for a much longer period. The precipitate formed at first will gradually redissolve. Now heat some of the solution in a flask, and expose another portion under the exhausted receiver of an air-pump. The excess of carbon dioxide will be seen to escape, and calcium carbonate will be deposited in each case (see also 11).

6. If carbon dioxide be led over heated metallic sodium, oxalate of sodium ($\text{Na}_2\text{C}_2\text{O}_4$) will be formed :—



7. When carbon dioxide is strongly heated with hydrogen it is reduced, water and carbon monoxide being formed according to the following equation, but the oxide is only completely reduced if the water formed is removed by a drying agent :—



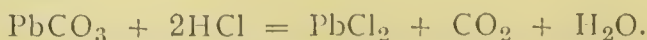
8. If carbon dioxide be heated to a very high temperature, as for example by exposing it to a strong disruptive discharge of electricity, its volume slowly increases, and the gas, which is no longer completely soluble in alkali, contains oxygen and carbon monoxide.

9. Carbon dioxide is reduced, as we have previously learnt, in the green parts of growing plants in sunlight.

281. The carbonates and bicarbonates. EXPERIMENT 215.

The properties of carbonates. 1. Endeavour to dissolve portions of various common carbonates in hot and cold water. Only the carbonates of sodium, potassium, and ammonium will dissolve. These all give solutions which are alkaline to litmus.

2. Add small quantities of various carbonates to dilute nitric acid. All will dissolve, giving off carbon dioxide freely, and neutralizing the acid if sufficient carbonate be employed. If other acids than nitric acid be used some carbonates may refuse to dissolve. For example, lead carbonate and hydrochloric acid would produce the insoluble lead chloride (PbCl_2) :—



3. Add some solution of a soluble carbonate to a solution containing any of the common metals except sodium, potassium, and ammonium.

A precipitate will fall, because all carbonates except those of the metals of the alkalis are insoluble.

The carbonates are a very important class of compounds, and many of them occur in nature. Insoluble carbonates may be prepared by precipitation as just described, and some are formed by the direct union of basic oxides with carbonic acid gas, in the presence of moisture, but never, it is believed, in its complete absence. The more important carbonates will be described separately in connexion with the metals.

EXPERIMENT 216. The preparation and properties of potassium bicarbonate. Dissolve a few grams of potassium carbonate in a very little water, place the solution in a small U tube, weigh the whole, and pass a slow current of carbonic acid gas through the solution. After a few hours, or days, reweigh the tube and its contents. It will be found to have increased in weight, showing that carbonate of potassium absorbs carbon dioxide.

If you continue the experiment for a sufficient length of time, crystals of a substance less soluble than potassium carbonate will separate. Collect these, and make the following experiments with them:—

(a) Dissolve some in water and warm the solution. Carbon dioxide will be given off freely.

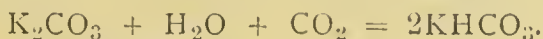
Make a similar experiment, using potassium carbonate. No gas will be evolved.

(b) Add a few drops of solution of mercuric chloride to solutions of the two carbonates. The new substance will give a yellowish-white precipitate, whilst the ordinary carbonate will give a red precipitate.

(c) Add some acid to the crystals. They will evolve carbon dioxide even more freely than the ordinary carbonates.

From these results it is clear that there are two carbonates of potassium.

Carbon dioxide (CO_2) forms a feebly acid solution when it is dissolved in water (Expt. 214, 3), and the simplest formula we can suggest for this acid is H_2CO_3 [why?], which represents carbonic acid as containing at least two atoms of hydrogen in each molecule. An acid having this composition would be likely to form two carbonates with a univalent metal like potassium, viz. a hydric carbonate KHCO_3 and a normal carbonate K_2CO_3 . Therefore it seems probable that the new substance is the *bicarbonate* KHCO_3 , formed according to the equation:—



Let us ascertain if this be true.

EXPERIMENT 217. To compare the proportions of carbon dioxide in carbonate of potassium and in the new substance.

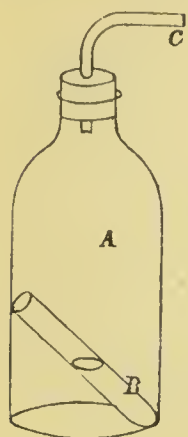


Fig. 103.

Weigh carefully about 0.3 gram of potassium carbonate. Introduce it into a small bottle *A* (Fig. 103), together with a tube *B*, containing some hydrochloric acid; connect *C* by a flexible tube with the eudiometer (see Fig. 41). Note the level of the water in the latter in the usual manner, open the tap, and after assuring yourself that the connexions are air-tight pour the acid from *B* on the carbonate. The gas set free will drive water from the eudiometer. When the action is complete, measure the volume of the water displaced by carbon dioxide. Then repeat the experiment, using the new salt. You will find that the latter gives a greater proportion of carbon dioxide than the normal carbonate.

Calculate what volume of carbon dioxide would be yielded by 0.3 gram of each of the two salts, on the assumption that their formulæ are K_2CO_3 and $KHCO_3$, and compare these volumes with the results of your experiments. If your work has been done well, you will find that the calculated volumes agree fairly well with those obtained experimentally.

*The normal carbonates**, with the exception of those of the alkali metals, are insoluble. Hence a solution of an alkaline carbonate may be used to detect the presence of metals in solutions.

The carbonates of the metals of the alkalis turn red litmus blue [verify this]. All carbonates are decomposed by mineral acids with evolution of carbon dioxide (see 281, 2).

Most carbonates, except those of the metals of the alkalis, are decomposed by heat; many are decomposed very easily. Hence oxides are made by igniting carbonates (see 343).

282. Carbon monoxide, carbonic oxide (CO). EXPERIMENT 218. To prepare carbon monoxide. 1. Heat a piece of combustion tube *A* (Fig. 85), about 50 cm. long, and packed with fragments of well-made charcoal, to redness. Then pass oxygen *slowly* over the red-hot carbon, and collect the product over water in a receiver *E*, after washing it with some strong solution of potash in a U tube. A colourless, tasteless gas will be obtained. This must

* A normal salt is one which contains no acidic hydrogen.

be insoluble in potash, for it was not absorbed by that substance in the U tube. Therefore it is not carbon dioxide.

Shake up a cylinder of the gas with lime-water. If it has been sufficiently washed with alkali, it will not give a precipitate of calcium carbonate.

Put a light to a jar of the gas. It will burn with a pale blue flame, and afterwards the contents of the cylinder will act on lime-water like carbon dioxide.

The new gas is carbon monoxide, formed according to the following equation :—



2. Repeat the above experiment substituting carbon dioxide for oxygen, and taking care to heat the carbon strongly. Carbon monoxide will again be formed :—



EXPERIMENT 219. Other modes of preparing carbon monoxide.

1. Heat about 100 grams of oil of vitriol with 20 grams of oxalic acid ($H_2C_2O_4, 2H_2O$) in a flask. Collect a little of the gas given off, over quicksilver, after expelling the air from the flask, and shake the gas with a little strong solution of potash. About half will dissolve; the residue will burn with a flame resembling that of carbon monoxide. Pass some of the mixed gases through some lime-water. You will find carbon dioxide to be present. This mixture of carbon monoxide and dioxide has been produced according to the following equation :—



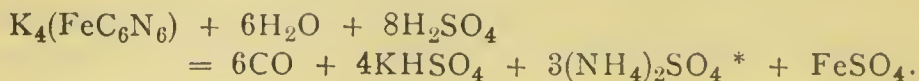
If the mixed gases be well washed with alkali, the carbon dioxide is removed. Consequently this reaction affords us a convenient method of preparing carbon monoxide.

2. Warm some sodium formate ($NaCHO_2$) with strong sulphuric acid. Carbon monoxide will be given off. The sulphuric acid may be supposed to liberate formic acid ($HCHO_2$), which is at once dehydrated :—



3. Heat potassium ferrocyanide ($K_4(FeC_6N_6), 3H_2O$) with a mixture of 3 parts of strong sulphuric acid and 1 of water. (The experiment may be tried on the small scale in a test tube.) The gas produced

usually has the odour of bitter almonds, owing to the presence of some prussic acid (HCN):—



4. Carbon monoxide is also formed, together with hydrogen, when charcoal or small coal is strongly heated in steam:—



Such a mixture of carbon monoxide and hydrogen is sometimes used as fuel when a clean smokeless flame is wanted, and is called *water gas*.

Carbon monoxide is frequently produced when carbon is used as a reducing agent, as, for example, in the making of phosphorus (248).

283. Some properties of carbon monoxide. We have seen that carbon monoxide is a colourless, odourless gas, and that it is nearly insoluble in water and in alkalis. Its density is slightly less than that of air, viz. 13.95. It has been liquefied. Its critical temperature is -140° , its critical pressure 35.5 atmospheres (130). The liquid boils at about -190° and it has been solidified. When carefully dried it is incombustible, but in the presence of traces of water-vapour it burns in air, and readily forms explosive mixtures with oxygen.

Carbon monoxide is highly poisonous, and it is found that when blood is shaken up with carbon monoxide, its oxygen is expelled and replaced by an equal volume of carbonic oxide. The carboxy-hæmoglobin formed is somewhat stable, and therefore it is difficult to resuscitate people poisoned by carbon monoxide. The fact that carbon monoxide is without odour, and therefore not readily detected by the sense of smell, adds to its dangerous character. This enables us to understand the deadly character of the fumes of a charcoal fire, and why it is dangerous to sleep very near a lime-kiln, in which carbon monoxide is generated, in calm weather. Air containing only 1 per cent. of this gas is said to be poisonous to man.

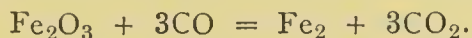
For nickel carbonyl, see 519.

* The ammonia may be detected by warming some of the contents of the test tube with excess of alkali. If part of the contents of the test tube be evaporated to dryness, and then strongly ignited, a residue containing iron rust will remain. The potassium sulphate may be extracted from this by water, and the potassium can be detected by the characteristic lilac colour which it communicates to the flame of a Bunsen burner.

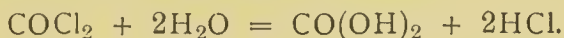
EXPERIMENT 220. To remove carbon monoxide from other gases. Introduce some solution of cuprous chloride (Cu_2Cl_2), by means of a pipette, into a tube containing carbon monoxide standing over quicksilver, and shake them together. The carbon monoxide will be absorbed gradually.

EXPERIMENT 221. To study the reducing power of carbon monoxide. Owing to its combustibility we should expect carbon monoxide to act as a reducing agent.

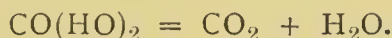
Pass carbon monoxide over some oxide of iron, or oxide of copper, heated in a hard-glass tube *A* (Fig. 85). Carbon dioxide will escape, and may be detected in the usual manner, whilst the altered colour of the residue will show that the oxide has been reduced * :—



Carbonic oxide combines with chlorine in sunlight. The product is *phosgene gas* or *carbonyl chloride* (COCl_2). Carbonyl chloride is also made by passing a mixture of chlorine and carbon monoxide through boiling antimony pentachloride, then over metallic antimony and into a well cooled tube, when the phosgene condenses to a liquid. It reacts with water according to the following equation :—



The carbonic acid ($\text{CO}(\text{OH})_2$) at once decomposes owing to its instability :—



It should be noticed that carbonic oxide does not react with bases, as carbon dioxide does; and that it does not form an acid solution in water.

284. The composition of the oxides of carbon. We have previously learnt (276) that the proportions of carbon and oxygen present in carbon dioxide have been determined by burning weighed quantities of carbon in carefully purified oxygen, and collecting and weighing the carbon dioxide formed. A more simple method, which the student himself may carry out, consists in burning a fragment of carbon in a fixed volume of oxygen, and observing the volume of the gas before and after the experiment. Then the composition by weight of carbon dioxide can be calculated from the observations made, and from the known densities of oxygen and carbon dioxide, viz. 16 and 22. The details of this method were given in connexion with Experiment 149.

* See also the 'blast furnace,' 489.

EXPERIMENT 222. To find the composition of carbon monoxide. The density of this gas, which is 14, and the fact that it contains only carbon and oxygen, suggest that its formula must be CO, for the molecular weight of a gas having this formula would be $12 + 16 = 28$, and its density 14, and all other possible combinations of atoms of carbon with atoms of oxygen would have a higher density than this. Its composition may be verified experimentally.

Introduce some carbon monoxide into a eudiometer over mercury. Ascertain its volume under standard conditions (63, 64). Add about an equal volume of oxygen, and note the volume of the mixture under standard conditions. Explode the gases by the electric discharge. Note the volume of the remaining gas as before. Submit it to the action of potash to remove the carbon dioxide formed in the explosion, and remeasure the residue of oxygen. Then calculate how much oxygen has been required to convert a known volume of carbon monoxide into a known volume of carbon dioxide, which, as we know, contains its own volume of oxygen.

The following example will make this clear :—

Let us suppose that 20.2 c.c. of carbonic oxide were taken at 0° and 760 mm., and that the volume became 40 c.c. after we added the oxygen. Then 19.8 c.c. of oxygen were added to 20.2 c.c. of carbonic oxide.

Let us further suppose that the volume of the gas left after the explosion was 30 c.c., and that potash absorbed 20 c.c. of carbon dioxide from this, leaving 10 c.c. of oxygen unused.

Then, since carbon dioxide contains its own volume of oxygen, we have produced 20 c.c. of carbon dioxide containing 20 c.c. of oxygen by adding 9.8 c.c. of oxygen to 20.2 c.c. of carbonic oxide.

It follows that the original 20.2 c.c. of carbonic oxide contained $20 - 9.8 = 10.2$ c.c. of oxygen.

Now the respective densities of carbon monoxide and oxygen are 14 and 16*.

Therefore the relative masses of 20.2 c.c. of carbonic oxide and 10.2 c.c. of oxygen are :—

$$20.2 \times 14 = 282.8 \text{ (carbon monoxide),}$$

$$10.2 \times 16 = 163.2 \text{ (oxygen).}$$

That is to say, 282.8 parts of carbon monoxide contain 163.2 parts of oxygen and $282.8 - 163.2 = 119.6$ parts of carbon.

* The exact values are nearly 13.9 and 15.9, but as the other measurements are only approximately correct, there would be no advantage in employing these exact values.

If we divide 163.2 by 8, the combining number of oxygen, and similarly divide 119.6 by 3, the combining number of carbon, we shall find that one equivalent of oxygen is united with very nearly two equivalents of carbon in carbon monoxide.

That is to say, 14 parts of the monoxide contain 8 parts of oxygen and 6 parts of carbon, for elements unite in exact multiples of their equivalent weights*.

The percentage composition and formula of the gas may be deduced from these numbers in the usual manner.

The chief compounds of carbon with sulphur were described in 207.

CARBON AND NITROGEN.

285. Potassium cyanide. If potassium carbonate mixed with carbon be heated to bright redness in contact with nitrogen, the product contains some potassium cyanide (KCN).

The same substance is formed when compounds containing nitrogen are heated with metallic potassium. On the large scale, animal refuse, such as hair or leather, is heated with scrap iron and potassium carbonate, and the product of this operation is treated with water, which extracts a fine yellow crystalline salt called *potassium ferrocyanide* ($K_4(FeC_6N_6) \cdot 3H_2O$). This salt is the source of potassium cyanide, and of most of the other cyanogen compounds. To prepare the former the dry ferrocyanide is heated with potassium carbonate, when it decomposes according to the following equation:—



The potassium cyanide of commerce, which is intensely poisonous, is a mixture of cyanide and cyanate of potassium extracted from the product of this operation.

N.B.—Experiments with cyanides should be made under the close supervision of a teacher.

EXPERIMENT 223. The properties of potassium cyanide. 1. To a drop or two of a dilute solution of potassium cyanide add some solution of ferrous sulphate, then a little ferric chloride, and finally, after warming, a slight excess of dilute hydrochloric acid. A precipitate of Prussian blue will fall.

2. Fuse a minute fragment of potassium cyanide with a particle of sodium thiosulphate. Dissolve the resulting potassium thiocyanate

* See equivalent weights, 84.

(KCNS) in water, and add a drop of solution of ferric chloride. A fine red colour will be imparted to the solution.

These reactions are characteristic of the cyanides and may be employed as tests, but if hydrogen cyanide be examined it must first be rendered alkaline.

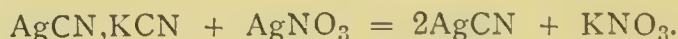
3. Heat some potassium cyanide strongly in a porcelain crucible, then add gradually some oxide of lead, or oxide of tin. The oxide will be reduced, it will yield a button of metal, and potassium cyanate (KCNO) will be formed.

This method of reducing metallic oxides is often made use of in the laboratory.

4. Dissolve a small fragment of potassium cyanide in water and add gradually some solution of silver nitrate. At first no precipitate will form, although silver cyanide is insoluble in water, because silver cyanide and potassium cyanide form a soluble double salt corresponding to the formula AgCN, KCN :—



but as soon as the amount of silver nitrate exceeds the proportion corresponding to this equation a precipitate of silver cyanide will be produced. Thus :—



The forming of this double cyanide is made use of in measuring the strengths of solutions containing hydrocyanic acid and cyanides.

Exercise. Prepare 200 c.c. of decinormal solution of silver nitrate (116).

Dissolve a gram of crystallized potassium cyanide, carefully weighed, in 20 c.c. of water.

Add the standard solution of silver nitrate, from a burette, to 10 c.c. of the solution of potassium cyanide (measure this from a burette and not by means of a pipette) until a permanent turbidity appears. This indicates that all the potassium cyanide has been converted into the double salt (KCN, AgCN) :—



Calculate the proportion of real KCN in the substance taken.

Alkaline cyanides are extensively used in extracting gold from gold-bearing rocks (see 555).

Potassium cyanide may be prepared free from cyanate by passing

hydrocyanic acid (HCN) into a solution of potassium hydroxide (KHO) in alcohol.

286. Hydrocyanic acid. EXPERIMENT 224. To prepare hydrocyanic acid (prussic acid) (HCN). This acid is liberated when a cyanide is distilled with dilute sulphuric acid, but it is usually made from potassium ferrocyanide. The experiment should be made under supervision, on a very small scale, and in a fume closet or in the open air.

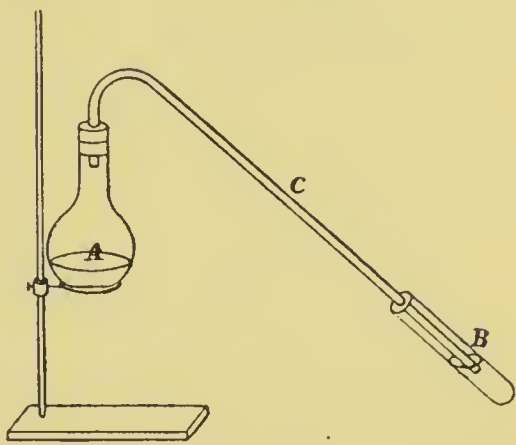
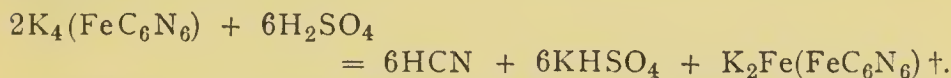


Fig. 104.

Place two or three decigrams of potassium ferrocyanide in a small flask or test tube *A*, add some dilute sulphuric acid, and attach a long delivery tube *C* to the mouth of the flask (Fig. 104), letting its end dip into a little cold water in *B*.

Distil part of the contents of *A*. The water in *B* will soon acquire the odour of 'bitter almonds,' and a bluish-white sediment will form in *A**:—



A very dilute solution of hydrocyanic acid is used in medicine under the name of *prussic acid* or *hydrocyanic acid*. Even in a diluted condition it is an extremely virulent poison.

EXPERIMENT 225. Some properties of hydrocyanic acid.

1. Add a little blue litmus to a drop or two of the dilute acid. The litmus will not be reddened.

2. Add a few drops of solution of ferrous sulphate to a little of the hydrocyanic acid made in Experiment 224, then slight excess of solution of potash and a little solution of ferric chloride; warm the

* Hydrocyanic acid should be smelt very cautiously as it is poisonous. It is a curious fact that about one person in four is unable to detect the odour of this substance. According to recent observers, if one molecular proportion of acid and ten molecular proportions of water are employed, only hydrogen cyanide, iron sulphate, and potassium sulphate are formed (Adie and Browning).

† Compare this reaction with that which occurs when carbon monoxide is made from the ferrocyanide (Expt. 219, 3).

mixture and acidulate it with hydrochloric acid. A precipitate of Prussian blue will be formed.

3. Add some solution of silver nitrate to a solution of hydrocyanic acid. A precipitate of silver cyanide (AgCN) will fall.

Add cold nitric acid to part of the product. It is insoluble, like the corresponding chloride.

4. Add a little solution of potash and then some yellow ammonium sulphide to a few drops of hydrogen cyanide. Evaporate the solution upon a water bath, dissolve the residue in a little water, and add a little solution of ferric chloride. A fine blood-red colouration, due to ferric thiocyanate ($\text{Fe}_2(\text{CNS})_6$), will be produced.

This reaction affords us a very delicate test for hydrocyanic acid.

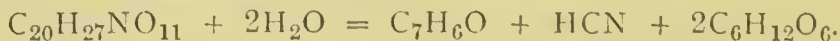
Solution of hydrocyanic acid is difficult to preserve even in the cold, especially if traces of alkali be present. This may depend to some extent on the marked volatility of the acid, but it is due partly to changes in which ammonia and formic acid are produced. Traces of hydrochloric acid retard the change.

Anhydrous hydrocyanic acid is a colourless liquid, lighter than water, which boils at about 26° . Both the liquid and its vapour, even if largely diluted with air, are deadly poisons. A single drop of pure hydrocyanic acid is said to be sufficient to cause instantaneous death, and therefore it should on no account be made by a student. It has been prepared by passing hydrogen sulphide over dry silver cyanide and condensing the acid by means of a freezing mixture:—



Hydrogen cyanide has been produced synthetically, mixed with other gases, by exposing a mixture of nitrogen and acetylene (C_2H_2) to the silent discharge of electricity (see ozone, 124).

Hydrocyanic acid can be obtained from various vegetable sources, such as the kernels of plums, cherries, and apricots, the blossoms of the sloe, and the leaves of the cherry laurel. It does not, however, always exist free in these substances. Thus bitter almonds contain a substance called *amygdalin* ($\text{C}_{20}\text{H}_{27}\text{NO}_{11}$)*, which when exposed to the action of a ferment known as emulsin (this occurs in sweet almonds) yields glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), hydrocyanic acid, and bitter almond oil ($\text{C}_7\text{H}_6\text{O}$); see *hydrolysis*, p. 340:—

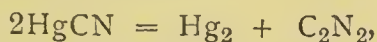


* This has been extracted from almonds by means of boiling spirit, after removing the oil by pressure.

287. Cyanogen (C_2N_2). This gas, which is a deadly poison, was discovered by Gay-Lussac in 1815. *It should NOT be prepared by a student.*

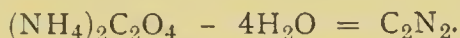
EXPERIMENT 226. To make cyanogen. A little cyanide of silver or cyanide of mercury is heated in a test tube *A* (Fig. 105), provided with a jet *T*, care being taken to ignite the gas as soon as it begins to escape at *T*.

The change which occurs when the mercuric cyanide is heated may be represented as follows:—



but paracyanogen is also formed and remains in *A* as a dark solid.

Cyanogen may be made by abstracting the elements of water from ammonium oxalate $((NH_4)_2C_2O_4)$ by treating it with phosphoric anhydride:—



Cyanogen is a colourless gas; it burns with a flame which exhibits two zones, viz. an inner peach-coloured zone, and an outer zone which shades off from blue to greenish-grey. The inner zone consists chiefly of carbon monoxide and nitrogen, whilst carbon dioxide is more plentiful in the blue region (Smithells and Dent).

It is partly decomposed by electric sparks, giving its own volume of nitrogen. It forms an explosive mixture with oxygen. It liquefies at -21° or under a pressure of five atmospheres at ordinary temperatures.

Paracyanogen (C_nH_n) is a condensed form of cyanogen; when strongly heated it yields cyanogen. Hence its density and the value of *n* in the above formula are unknown.

OTHER COMPOUNDS OF CYANOGEN.

288. When hydrocyanic acid is treated with chlorine a volatile substance with an unpleasant pungent odour is formed. This is cyanogen chloride ($CNCl$). If excess of chlorine be present it gradually polymerizes in sunlight, forming a white crystalline solid, cyanuric chloride ($C_3N_3Cl_3$).

A bromide and an iodide of cyanogen are also known. The latter sometimes occurs in crude iodine. It may be made by shaking together mercuric cyanide and iodine in a securely closed bottle; fine

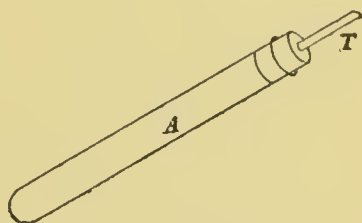
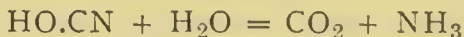


Fig. 105.

colourless needles of iodide of cyanogen are produced, which appear and disappear on different parts of the bottle in ever varying forms.

289. Cyanic acid and cyanuric acid. The resemblance between the compounds of cyanogen and those of the halogens, for example, the acid character of their hydrides, the insolubility of their silver salts, and the tendency of metallic cyanides and halides to form double compounds, such as the double cyanide of potassium and silver*, may have led the student to suspect the existence of cyanogen compounds, containing oxygen, analogous to hypochlorites, chlorates, or perchlorates. Such a compound exists in cyanic acid (HCNO or NC.OH), which may be made by distilling cyanuric acid ($\text{H}_3\text{C}_3\text{N}_3\text{O}_3$), or by heating urea with phosphoric oxide, and its salts, the cyanates, have already been alluded to (285).

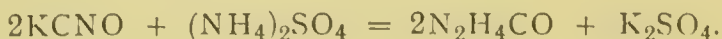
Warm some dilute sulphuric acid with a little solution of potassium cyanate. Notice that a pungent gas, together with carbon dioxide, is given off, and that ammonia can be detected in the solution. This is explained by the fact that free cyanic acid readily interacts with water according to the following equation:—



A polymeride of cyanic acid, cyanuric acid ($\text{N}_3\text{C}_3\text{O}_3\text{H}_3$), is formed when cyanuric chloride ($\text{N}_3\text{C}_3\text{Cl}_3$) (288) is acted on by water. It is a crystalline acid forming a trisodium salt ($\text{N}_3\text{C}_3\text{O}_3\text{Na}_3$).

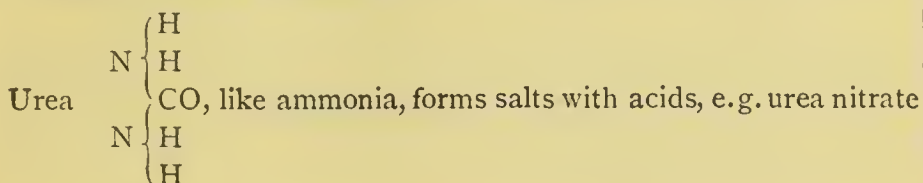
Cyanates. When potassium cyanide is prepared by igniting ferrocyanide of potassium with potassium carbonate, potassium cyanate (KCNO) is one of the products. This salt is also produced when potassium cyanide is oxidized in the air, or by heating potassium cyanide or ferrocyanide with an oxidizer such as manganese dioxide. The most interesting of the cyanates is ammonium cyanate. As previously explained, this salt was converted into urea by Wöhler in 1828.

EXPERIMENT 227. To prepare urea. Dissolve one molecular proportion of ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) in a little water, add two molecular proportions of potassium cyanate (KCNO) also in solution, and evaporate the mixture to dryness on a water bath. The residue will contain urea and potassium sulphate:—



* See also ferrocyanides, ferricyanides, and mercuric iodide.

Digest the residue with warm alcohol, filter the alcoholic solution from the potassium sulphate, and evaporate the filtrate on a water bath till it yields crystals on cooling.



((N₂H₄CO), HNO₃). When urea is strongly heated it gives off ammonia, leaving a residue of cyanuric acid.

Thiocyanic acid. Potassium thiocyanate is formed in the test for hydrocyanic acid and cyanides given in Experiment 225, 4. Ammonium thiocyanate (NH₄S.CN) is converted into a thio-urea (N₂H₄CS) when it is heated to 170°.

290. Ferrocyanides and ferricyanides. The compounds of cyanogen exhibit a remarkable tendency to form polymerides, and to produce double salts such as the double cyanide of silver and potassium. The ferrocyanides and ferricyanides afford us very interesting illustrations of the latter quality. Ferrocyanide of potassium is made on the large scale by fusing together waste nitrogenous material, scrap iron, and carbonate of potassium (285), and is the source of many compounds containing cyanogen; it is also formed when a ferrous salt is added to potassium cyanide in the presence of alkali:—



and it might very well be supposed to be merely a double cyanide of iron and potassium corresponding to the formula 4KCN, FeC₂N₂, 3H₂O, analogous, let us say, to alum (431).

If this view be correct, the salt should exhibit the ordinary reactions of potassium and iron. That is to say, for example, it should yield a precipitate of ferrous hydroxide with solution of soda, like ferrous sulphate and the other ferrous salts. But if the experiment be made it will be found that ferrocyanides do not respond to the ordinary tests for iron in the ferrous state (see 499).

Again the salt cannot be a cyanide, for when some solution of potassium ferrocyanide is added to copper sulphate, it does not yield a precipitate of copper cyanide (Cu(CN)₂), but one which differs from copper cyanide in appearance, and which corresponds, in composition, to the formula Cu₂FeC₆N₆. We may therefore suppose that the

precipitate in question is the cupric salt of an acid having the formula $\text{H}_4\text{FeC}_6\text{N}_6$, and that it is formed from the corresponding potassium salt $\text{K}_4\text{FeC}_6\text{N}_6$ according to the following equation :—



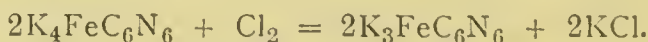
This view of the nature of potassium ferrocyanide is supported by the fact that other compounds containing the radicle FeC_6N_6 are known, and that ferrocyanic acid itself has been obtained as a solid, which rapidly becomes blue in air.

1. To a solution of ferrocyanide of potassium add some solution of ferrous sulphate. A whitish precipitate will fall which quickly becomes blue by oxidation.

2. Add a few drops of potassium ferrocyanide to excess of a solution of ferric chloride. A dark blue precipitate will fall, which consists chiefly of Prussian blue.

The behaviour of potassium ferrocyanide with weak and with strong sulphuric acid has been discussed in 282 and 286.

EXPERIMENT 228. Ferricyanide of potassium. Dissolve a few grams of ferrocyanide of potassium in a little water, and pass chlorine through the solution. When the change of colour which takes place appears to be complete, test a little of the solution with ferric chloride from time to time, and when the solution no longer yields a dark blue precipitate with the ferric salt, evaporate it till it yields red crystals of potassium ferricyanide ($\text{K}_3\text{FeC}_6\text{N}_6$ or $\text{K}_6\text{Fe}_2\text{C}_{12}\text{N}_{12}$) together with some chloride of potassium. The following equation indicates the nature of the change :—



Add a solution of one of the red crystals to some solution of ferrous sulphate. A deep blue precipitate will form. The acid of these salts, ferricyanic acid ($\text{H}_3\text{FeC}_6\text{N}_6$ or $\text{H}_6\text{Fe}_2\text{C}_{12}\text{N}_{12}$), has been prepared, in the form of lustrous brownish green needles, by adding concentrated hydrochloric acid to a cold concentrated solution of potassium ferricyanide.

THE CHIEF COMPOUNDS OF CARBON AND HYDROGEN.

291. Methane, marsh gas (CH_4). **EXPERIMENT 229. To prepare marsh gas.** 1. Mix some sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$), previously dried, with excess of caustic soda, add some quicklime to prevent the mixture from fusing when it is heated; heat the mixture

strongly in a copper tube provided with a delivery tube, and collect the gas evolved over water. The following reaction occurs:—



2. Pour a little iodide of methyl (CH_3I) into a flask containing a wet zinc-copper couple (125, 2, c) and provided with a delivery tube. Methane will soon escape from the delivery tube, and may be collected as before.

EXPERIMENT 230. Some properties of methane. We have seen that methane is a colourless, odourless gas insoluble in water.

Apply a flame to a jar containing methane. The gas will burn. Notice that its flame is non-luminous like that of hydrogen.

Methane is difficult to liquefy, but it forms a liquid which boils at -164° and has been frozen. It is one of the lightest gases, and contains a larger proportion of hydrogen than any other compound. Mixed with air it forms the 'fire-damp' of coal mines*, and recently raised coal sometimes contains twice its volume of a gas which very largely consists of methane. Marsh gas is produced in the decay of organic matter. Hence it occurs in marshy districts, and is frequently present in the bubbles which rise to the surface of stagnant ponds. It is an important constituent of coal gas.

Methane does not combine with chlorine or the other more active elements, but its hydrogen may be replaced by chlorine, when it forms the following interesting series of compounds:—

Monochloromethane.	.	.	.	CH_3Cl
Dichloromethane	.	.	.	CH_2Cl_2
Trichloromethane	.	.	.	CHCl_3
Tetrachloride of carbon	.	.	.	CCl_4

The third of these substances (CHCl_3) is *chloroform*, the anæsthetic. It is easily made by distilling bleaching powder with alcohol and water. The student should take care to examine a specimen of this important compound. It is a volatile liquid with a pleasant characteristic odour, and is a useful solvent.

292. To analyse a gaseous hydrocarbon. **EXPERIMENT 231. To find the composition of methane.** 1. Collect some marsh gas over mercury in a eudiometer (Fig. 41), and find its volume at 0° and 760 mm. as in previous similar experiments (63, 64).

Let its volume at 0° and 760 mm. be 12 c.c.

* The fine coal dust which floats in the air of such places is a contributing cause to the terrible explosions which occur in coal mines.

Add about three times as much oxygen, and find the volume of the mixture under standard conditions as before. Let its volume be 48 c.c.

Explode the mixture, taking the usual precautions. The residue will consist of carbon dioxide, oxygen, water-vapour *, and a negligible volume of water in the liquid state.

Let the volume of the carbon dioxide and oxygen at 0° and 760 mm. be 24 c.c.

Treat the residue with potash to remove carbon dioxide, and measure the residual oxygen.

Let its volume at 0° and 760 mm. be 12 c.c.

Then 12 c.c. of marsh gas when exploded with 36 c.c. of oxygen have consumed 24 c.c. of oxygen, and produced 12 c.c. of carbon dioxide together with some water.

Now 12 c.c. of carbon dioxide contain 12 c.c. of oxygen, and 24 c.c. of oxygen were used in our experiment.

Therefore, as only water and carbon dioxide are formed, 12 c.c. of oxygen must have obtained 24 c.c. of hydrogen from 12 c.c. of marsh gas.

Now the density of marsh gas is 8 †.

Therefore 12 c.c. of marsh gas, weighing $\frac{0.09}{1000} \times 8 \times 12 = 0.00864$ gram, contain 24 c.c. of hydrogen, weighing $\frac{0.09}{1000} \times 24 = 0.00216$, together with $0.00864 - 0.00216 = 0.00648$ gram of carbon.

Its percentage composition may be calculated from these data.

In practice the results obtained would not correspond so closely to the truth as the hypothetical numbers which form the basis of the above calculation, for it is not possible to obtain the highest degree of accuracy by the method of analysis here described. The approximate results obtained from such an experiment can, however, be controlled, for we know that the equivalent weights of carbon and hydrogen are nearly in the ratio of 3 to 1 (see 84).

2. The composition of marsh gas may also be demonstrated by passing sparks of electricity through a known volume V of the gas, until it ceases to expand. When this is done carbon is deposited, and the volume of the gas becomes $2V$. The gas produced is hydrogen, for it combines with half its volume of oxygen, forming water.

* When a gas saturated with water vapour is measured we deduct the vapour tension of water at t from the pressure of the gas. Tables of vapour tensions will be found in the larger works on chemistry.

† Approximately.

Therefore 1 volume of marsh gas contains 2 volumes of hydrogen. Then the densities of marsh gas and hydrogen being known it is easy to calculate the corresponding masses of the carbon and hydrogen.

293. Ethane and the paraffins. EXPERIMENT 232. To make ethane (C_2H_6). Prepare a zinc-copper couple, add to it, whilst damp, some ethyl iodide (C_2H_5I). A colourless gas will be evolved which will burn with a luminous flame. This gas has been analysed. Its formula is C_2H_6 . Like methane, it does not enter into direct combination with chlorine or other elements, but gives rise, by substitution, to such compounds as chloride of ethyl (C_2H_5Cl) and dichlorethane ($C_2H_4Cl_2$); and alcohol ($C_2H_5(HO)$), as we shall presently learn, is one of its derivatives.

Many other similar hydrocarbons are known. Thus we have propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), and hexane (C_6H_{14}). These may be prepared by similar reactions to those mentioned above, and all exhibit very similar chemical properties. The members of this group of compounds are known as the paraffins, and paraffin wax* consists largely of the higher members of the series.

294. Homologous series. If the formulæ of the above-mentioned hydrocarbons are arranged in a series in the order of their molecular weights, it will be found that each term of the series differs from its predecessor by a constant increment, viz. by one atom of carbon and two of hydrogen, and that the composition of all the members of the series corresponds to the general formula C_nH_{2n+2} . Thus we have:—

Methane	.	.	.	.	.	.	.	CH_4
Ethane	.	.	.	.	.	.	.	C_2H_6
Propane	.	.	.	.	.	.	.	C_3H_8
Butane	.	.	.	.	.	.	.	C_4H_{10}
Pentane	.	.	.	.	.	.	.	C_5H_{12}
Hexane	.	.	.	.	.	.	.	C_6H_{14}
General formula for the series	.	.	.	.	.	.	.	C_nH_{2n+2}

The successive members of this series of compounds not only differ regularly in regard to their composition and molecular weights, but also exhibit somewhat regular changes in their physical properties

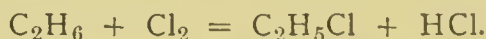
* From *parum affinis*, which implies low or small affinity, on account of the inertness of paraffin wax.

as we proceed from the lower to the higher members, as may be gathered from the following table:—

<i>Name.</i>	<i>Molecular Weight.</i>	<i>Density.</i>	<i>Boiling-point.</i>
Methane . .	16	8 (H = 1)	Gas
Ethane . .	30	15 „	„
Propane . .	44	22 „	„
Butane .	58	0.60 (H ₂ O = 1)	1°
Pentane . .	72	0.628 „	37°
Hexane . .	86	0.660 „	69°
Heptane . .	100	0.700 „	98.5°
Octane . .	114	0.719 „	125°

Some idea of the chemical similarity of the paraffins may be gathered from what follows.

When ethane, mixed with chlorine, is exposed to diffused sunlight, its hydrogen is more or less replaced; among the products of the change is a substance called ethyl chloride (C₂H₅Cl):—



If this substance be heated with dilute alkalis under pressure, a compound which has the formula C₂H₅O is formed together with potassium chloride:—



This latter compound is alcohol or spirit of wine. When it is oxidized it is converted into acetic acid—the acid of vinegar. Now if propane be similarly treated, it also will yield a chloride, an alcohol, and an acid; and, in a general way, the same may be said of the other members of the series, though the student must not conclude from this that such derivatives have been actually prepared in every case.

Since each hydrocarbon can thus give rise to a chloride, an alcohol, and an acid, it will be understood that besides the various homologous

series of hydrocarbons, for there are several, there are similar series of chlorides, alcohols, and acids, but further information on this subject must be sought in a treatise on organic chemistry.

295. Oils and Fats. (a) **The paraffins in commerce and the arts.** At various places in North America, at Baku in south-eastern Russia, and elsewhere, gaseous mixtures escape from the earth which usually contain large proportions of hydrogen and methane, together with smaller quantities of other hydrocarbons; and mineral naphtha or petroleum is obtained in large quantities from natural oil-springs, or by means of borings, in the same localities. The origin of these substances is not definitely understood. It has been supposed that they may have been produced by the decomposition of organic matter at the lower levels of the earth's crust, but Professor Mendeléeff, the eminent Russian chemist, suggests that they may owe their origin to the action of water on metallic carbides formed in past ages.

Crude petroleum is lighter than water; it varies in composition and in consistency, and consists mainly of hydrocarbons of the paraffin type. It is not usually employed as an illuminating agent, or for fuel, as it comes from the springs, but is divided, by fractional distillation (p. 24), into various mixtures. Some of the more volatile of these, which are known in commerce under such names as *petroleum ether*, *gasoline*, and *petroleum spirit*, are used for cleaning purposes and in the making of varnishes, on account of their solvent power. The fractions which boil at somewhat higher temperatures are used as illuminants, and those which distil above 300° are used as lubricants. 'Vaseline' is extracted from the least volatile portions.

Paraffin wax consists of mixtures of solid paraffins extracted from the oil produced by distilling bituminous shale. It is found native in the form of fossil wax.

(b) **Oils and fats of vegetable and animal origin—fatty acids—soap—glycerine.** The commoner oils and fats are mostly neutral substances which do not dissolve in water and which, owing to their low density (p. 25), float upon its surface. The oils are, as a rule, derived from vegetables, whilst the fats, which when melted form oils, are mostly, as in the case of suet, tallow, beeswax, and spermaceti, more or less solid, but animal oils also are known. The common oils and fats are not volatile, but when distilled undergo destructive distillation (p. 25).

These vegetable and animal fats differ markedly from the paraffins,

which are found as said above in North America, south-eastern Russia and elsewhere in their chemical constitution. For example, the latter when burnt yield water and carbon dioxide in proportions which show that they contain no other constituents than hydrogen and carbon, whilst the former are known to contain oxygen as well as hydrogen and carbon. Again, the latter when heated with solution of potash or soda remain unaffected. The former, on the other hand, yield soap and glycerine when similarly treated.

We can understand the nature of these vegetable and animal fats best if we first get a clear idea of the nature of soap, for which purpose the student must provide himself with a little oleic acid ($\text{HC}_{18}\text{H}_{33}\text{O}_2$) and stearic acid ($\text{HC}_{18}\text{H}_{35}\text{O}_2$), these being two insoluble acids obtained from various oils and fats.

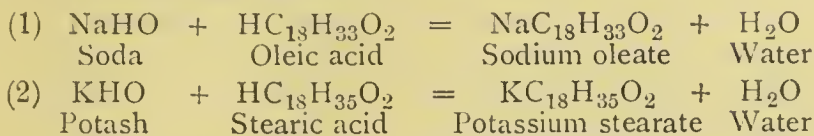
Hard soap. Warm a few drops of oleic acid with two or three cubic centimetres of solution of soda. When it is dissolved, add a drop or two of the solution to a larger volume of water, and observe that it froths as freely as a solution of soap when well shaken. To the rest of the solution add some common salt, or pour the soap solution into some strong brine. Collect the precipitate which falls on a filter, press it to remove the brine, and examine it to find whether it feels like soap, whether a minute portion dissolved in distilled water gives a frothing solution, and whether it behaves like soap with hard water (11).

Retain the rest of your soap for a subsequent experiment.

Soft soap. Warm a piece of stearic acid about half as big as a filbert with two or three cubic centimetres of rectified spirit, and cool the solution. Notice that the acid is redeposited in tufts of feathery crystals. Boil another portion of the acid with a little *potash* dissolved in alcohol and again cool the solution, and notice whether you again obtain crystals, or whether a gelatinous mass resembling soft soap is formed. In the latter case dilute a few drops of the product with water—reserving most of it, however—and test as before to find if the liquid behaves like a solution of soap. Try, also, if you can obtain a hard soap by adding salt to the solution of soft soap.

On considering the results of the above experiments, you will recognize that soap may be made by processes closely resembling those employed in preparing an ordinary salt, such as common salt, NaCl (p. 143, 9), or lead acetate (p. 142, 5), from their acids by the action of the metallic oxide, PbO , or the hydroxide, NaOH .

If this view be correct, we might represent the making of the two soaps by the following equations :—



Showing that the soaps you have prepared consist respectively of oleate of sodium and stearate of potassium.

To confirm this hypothesis, ignite a little of the sodium soap strongly on a bit of platinum foil till a white saline residue remains; add a drop of hydrochloric acid to this, warm it till it is dry, and find if it tastes like common salt. Further, dissolve what is left of the two soaps in water, add diluted sulphuric acid cautiously till it is in slight excess, and warm gently. Notice whether the soap made from oleic acid gives an oil which is permanently liquid like oleic acid, and whether the other soap gives an oil which solidifies on cooling like stearic acid. You will find that the acid of a soap can be recovered from it, much as hydrochloric acid can be recovered from common salt.

Finally, see if you can obtain fusible fatty substances from commercial hard and soft soap respectively by the action of acids, and ignite small fragments of these soaps and find if the metals present in them are sodium or potassium. This may be done by moistening the residues with hydrogen chloride and holding them in the flame of a bunsen burner, as sodium gives a strong yellow colouration and potassium a lilac colouration to the flame when thus tested.

Soap, then, is a kind of salt containing sodium in the case of hard soap and potassium in that of soft soap.

Soap is not made on the large scale by the direct action of acids with soda or potash, but from oils and fats. These oils as a rule are mixtures; hence ordinary soap is usually a mixture of several salts, such as those prepared in the above experiments.

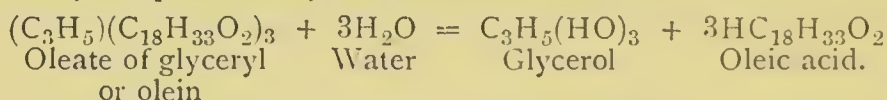
The process by which soap is prepared from oil is termed *saponification*. It consists in boiling any common oil or fat with a strong solution of alkali, and then 'salting out' the soap if it be a soda soap or evaporating the solution. The latter method is especially employed in making soft soap.

The experiment which illustrates the nature of these interesting substances in the simplest way is not very easy for the student to carry out, but it is performed on the large scale, chiefly with solid fats, by the makers of candles and glycerine.

If olive oil be heated with steam to 200° or higher, it is converted into a mixture of fatty acids, chiefly oleic acid, and glycerine which remains dissolved in the water at the end of the process.

Most of the common oils give oleic acid when thus treated, though other acids also are formed, as in the case of palm oil. Solid oils or fats, such as suet, give chiefly stearic acid. In all cases the base produced is glycerine.

Now glycerine, or glycerol, is the hydroxide of a tribasic radicle glyceryl (C_3H_5), viz. $C_3H_5(HO)_3$, and oleic acid is a monobasic acid having the formula $HC_{18}H_{33}O_2$. And chemists conclude that the source of these substances is oleate of glyceryl, $C_3H_5(C_{18}H_{33}O_2)_3$, and that they are produced by such reactions as :—



In fact, they regard the constituent of the oil which yields oleic acid and glycerine as a sort of salt*, analogous to the inorganic salts but containing the radicle glyceryl in place of a metal.

The other constituents of olive oil and other fats behave in a similar manner. Thus, if a solid fat, such as suet, is acted on by superheated steam we obtain, besides some oleic acid and glycerol, a great deal of stearic acid, $HC_{18}H_{35}O_2$, and hence suppose that the solid fat contains much stearate of glyceryl or stearin, $C_3H_5(C_{18}H_{35}O_2)_3$. Again, palm oil yields palmitic acid, $HC_{16}H_{31}O_2$, and so must contain palmitate of glyceryl or palmitin, $C_3H_5(C_{16}H_{31}O_2)_3$.

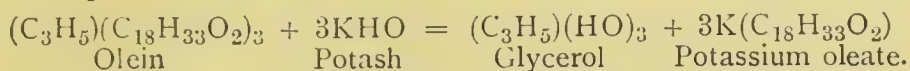
These three substances, olein, stearin, palmitin, occur very widely; olein being the liquid constituent of most of the commoner non-drying fats and oils from vegetable and animal sources; stearin the chief component of solid animal fats such as suet, whilst palmitin occurs in palm oil, &c. But other similar compounds also occur. Thus spermaceti contains cetyl palmitate $(C_{16}H_{33})(C_{16}H_{31}O_2)$, and beeswax is a mixture of a free acid, cerotic acid, $HC_{27}H_{53}O_2$ with myricyl palmitate $(C_{30}H_{61})(C_{16}H_{31}O_2)$.

Soap is prepared on the large scale from the commoner fats and oils, such as palm oil, olive oil, &c., by boiling them repeatedly with strong alkaline solutions. If potash is used the product is boiled down and is known as soft soap. But soda soaps or hard soaps are 'salted out' as in the above experiments.

The following equation represents the change that occurs in the case

* Such salts are called *esters*.

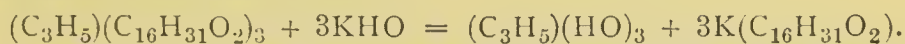
of olein. But as most natural fats are mixtures, the soaps produced from them are mixtures also; the most common constituents being oleates, palmitates, and stearates of sodium or potassium:—



The glycerine produced in soap factories was formerly lost, but is now largely recovered.

By making the following experiment the student will gain a clearer idea of the meaning of the above statement:—

Dissolve about 25 grams of caustic potash in about 25 c.c. of water; add 30 grams palm oil and heat them together with constant stirring for half an hour or so on a water bath. Dilute the product with 500 c.c. of hot water and remove any undecomposed oil by means of a separator if necessary. You have now an aqueous solution containing soft soap and glycerol.



Add solution of hydrochloric acid to this solution to decompose the soap and liberate the palmitic acid.



On cooling, a cake of the impure acid will rest above the watery part. If this cake be freed from water and the product strongly pressed on porous material to remove the liquid part, and then crystallized from spirit and dried on a porous plate in the sun, you may obtain palmitic acid nearly pure. It melts at 62°.

The glycerine may be identified by evaporating the watery liquid from the above process to dryness on a water bath, after removing the cake of palmitic acid, warming the residue with rectified spirit, and evaporating the solution to get rid of the spirit, when a residue of impure glycerol will remain.

If the student compares the formulae of palmitic and stearic acids with that of acetic acid,



he will see that they belong to an homologous series (p. 335) having the general formula $HC_nH_{2n-1}O_2$.

Many other members of this series of fatty acids are well known to students of organic chemistry.

Linseed oil. The oils we have been considering all belong to the

class known as non-drying oils, but there are others, such as those which are obtained from the seeds of the poppy, hemp, and linseed, which, when exposed to the air, absorb oxygen and gradually become resinous, and which accordingly are employed for preserving wood. These drying oils are compounds of glyceryl with an acid known as *linoleic acid*, $\text{HC}_{18}\text{H}_{31}\text{O}_2$, which, it will be noticed, contains a smaller proportion of hydrogen than any of those previously mentioned.

Soap and Hard Water. The destruction of soap by water containing calcium or magnesium becomes intelligible now we understand that soap is a salt. What happens when soap is added to water containing these or certain other metals is this—that an insoluble oleate or stearate is precipitated. Thus if the water contains calcium chloride the change may be written for sodium stearate:—



No soap can exist in the water as long as any calcium remains. It is all precipitated as calcium stearate.

This may be verified by adding soap to a neutral solution of calcium, collecting the precipitate, draining it, and decomposing it with acid, when the fatty acid of the soap will be obtained.

Butter is a mixture of several non-volatile fats, viz. stearin, palmatin and the glyceryl compound of myristic acid, together with volatile compounds of butyric acid and other allied acids.

Milk contains, besides the fats which can be removed as cream and converted into butter, a kind of sugar known as milk sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, H_2O . To obtain this, curdle some milk and remove the casein and fatty matter thus thrown down by filtering*. If you then concentrate the watery liquid which remains, you may obtain, on cooling, crystals of milk sugar. You will find it to be less sweet and less soluble than cane or grape sugar.

296. Alcohol, its isolation, some of its properties. EXPERIMENT 233. To produce spirit of wine or alcohol ($\text{C}_2\text{H}_6\text{O}$). Distil a quarter of a pint of inexpensive sherry, collect the first half, and redistil it from a little quicklime in a retort. The product will consist of a colourless liquid, which boils at a lower temperature than water and possesses a hot taste. Add a little iodine to a drop or two of this spirit, then solution of potassium hydroxide until the iodine is destroyed, and warm gently. A yellow

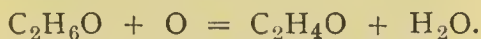
* When collected, drained, pressed, and matured, these constitute cheese.

precipitate will form, and the peculiar odour of iodoform may be observed*.

Add some anhydrous copper sulphate (539) to a little of the spirit. The copper salt will be turned blue, for the spirit still contains water.

Pure spirit, or nearly pure spirit, which is called *absolute alcohol*, is prepared by repeatedly exposing dilute spirit, in larger quantities than in the above experiment, to the action of fresh portions of quicklime (CaO).

EXPERIMENT 234. Some properties of alcohol. Like all combustible substances, alcohol has considerable powers as a reducing agent. Add a little sulphuric acid to some solution of potassium bichromate, and warm the mixture with a few drops of alcohol. It will turn green, owing to the reduction of the chromate, and at the same time the alcohol (C₂H₆O) will be oxidized to aldehyde (C₂H₄O), which may be recognized by its peculiar odour:—



‘Absolute alcohol,’ which should not contain less than 99.5 per cent. of alcohol (C₂H₆O), is a colourless liquid, lighter than water (its density is 0.806 at 0°), which boils at about 78°. It is very difficult to freeze, and is therefore used for thermometers in cold climates. In large doses it is a poison. It is chiefly obtained by fermenting solutions containing sugar.

297. Alcoholic fermentation. **EXPERIMENT 235. To prepare alcohol from sugar.** Add a small quantity of brewers’

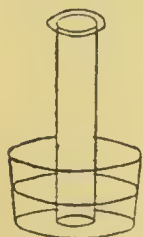


Fig. 106.

yeast† to a few litres of a dilute aqueous solution of cane sugar or of grape sugar, place the greater part of the mixture in a capacious flask, and the rest in a small cylinder, and invert the cylinder in a basin of water (Fig. 106). Stand both vessels aside at a temperature of about 20°. Before long, fermentation will set in, and a gas will be given off which will gradually displace the liquid from the cylinder. If this gas be tested, it will be found to be carbon dioxide. It will also become

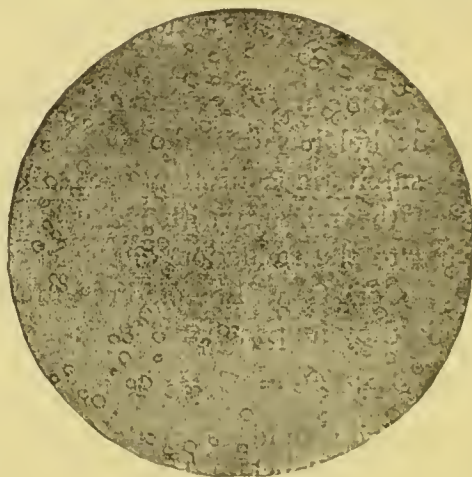
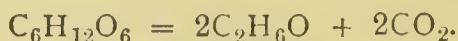
evident that the yeast increases in quantity during the process.

After 20 or 30 hours, strain the liquid from the yeast, distil off about

* This is a useful test for alcohol; by its aid 1 part of alcohol can be detected in 2000 parts of water; but some other compounds give similar reactions, which limits its value.

† Add a little of the ash of incinerated yeast and a trace of an ammonium salt.

one third of it, treat the distillate with quicklime, as previously described, and apply the iodoform test (296) to the product *. If grape sugar be employed the change may be represented by the following equation, but alcohol is not the sole product:—



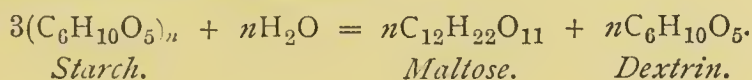
YEAST CELLS.

If the yeast be examined under the microscope, it will be found to consist of rounded, nearly transparent cells. When these are placed in a suitable solution, at about 25° , they produce buds which grow and finally separate from the parent cell. The production of spirit from sugar is known to be dependent on the action of these cells, since it can only be made to occur with solutions of sugar in which they are growing, or with solutions to which the juice of fresh yeast has been recently added. It should be said that cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) does not itself ferment, but that ordinary yeast contains ferments which are able to convert cane sugar into a fermentable sugar.

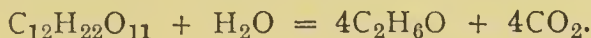
298. Wine, beer, &c. Wine is prepared by fermenting the sugar of grape juice, and as a rule the change is brought about by organisms present in the air, or on the grapes, or their stalks. It seems probable that the different flavours of the wines produced in different localities does not depend solely on the different varieties of grapes employed, and the mode of culture followed, but partly on the character of the fermenting organisms.

* Undue exposure of the weak solution of alcohol to the air may result in the forming of acetic acid by another fermentation (see 299).

Beer is made from malt and hops, or from substitutes for these. To make malt, barley is soaked in water, and spread in layers, in a moist atmosphere and at a suitable temperature, till it germinates. Then, at a certain stage, the grains are heated sufficiently to stop their growth; during germination a ferment called *diastase* is formed. The malt is crushed, and digested with water at about 65°. A change sets in, and the *starch* $(C_6H_{10}O_5)_n$ in the malt is converted, under the influence of the *diastase**, into a substance called *dextrin* and a fermentable sugar called *maltose* :—



The solution is then boiled to stop the action of the diastase, hops are added, and finally, when its temperature is suitable, some yeast; whereupon the maltose undergoes alcoholic fermentation :—



Beer contains from 3 to 6 per cent. of alcohol, together with some dextrin, sugar, glycerol, fusel oil, and other substances to which its colour and flavour are partly due. A certain amount of carbon dioxide is retained in solution, and contributes to its flavour.

Hydrolysis. Changes like that in which starch is converted into maltose and dextrin are termed *hydrolyses*. It will be noticed that the compound hydrolyzed assimilates water, and is resolved into two new substances; see also amygdalin, p. 228.

Rectified spirit is the name given to a strong spirit purified to a great extent from fusel oil.

Proof spirit contains about 50 per cent. by weight of alcohol. Spirit is described as *over proof* if it be stronger than this, and as *under proof* if it be weaker.

The term ‘proof spirit’ is said to be derived from a former practice of testing the strength of spirituous liquors by moistening gunpowder with the spirit, and applying a light. When a weak spirit is treated in this way, it burns away, leaving the gunpowder so damp that it does not ignite; a strong spirit ignites the gunpowder. Spirit which was just strong enough to ignite gunpowder was called ‘proof spirit.’

Brandy and whisky are about as strong as proof spirit. Port and

* Diastase is not an organized ferment capable of reproducing itself like yeast. It belongs to a class of ferments called ‘enzymes.’

sherry contain about 20 per cent. of alcohol, whilst a light claret contains about 7 per cent. and lager-bier as little as 3 per cent. of alcohol.

Methylated spirit. Alcohol is used very largely in the manufacture of such substances as ether and chloroform and as a solvent. Hence the heavy duty charged upon this substance, in England, seriously handicaps various industries. This difficulty has been, to some extent, removed by an Act of Parliament, which permits the manufacture and sale of a mixture of raw spirit with 10 per cent. of wood spirit and a little paraffin oil called *methylated spirit*. Such a mixture is quite unfit for use as a beverage, but it can be employed in many manufacturing processes. If methylated spirit is distilled from potash and afterwards dehydrated with quicklime, as already described, it may be used for many of the experiments described in this book, and it will be found to be much less expensive than rectified spirit.

Bread and fermentation. Bread is made from flour by mixing it with water and a little yeast, and placing the dough in a warm place that it may ferment. Part of the starch is changed into sugar which yields alcohol and carbon dioxide, and thus the mass of dough becomes honeycombed with small bubbles of gas. When the dough has 'risen' sufficiently in consequence of this change, it is heated in an oven; the heat checks the fermentation and expands the contents of the bubbles, thereby making the bread sufficiently light and porous.

299. Acetic acid. Vinegar ($\text{HC}_2\text{H}_3\text{O}_2$). Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. Citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$. When 'aldehyde' (p. 342 *a*) is used to reduce a silver salt, or exposed to the air in contact with platinum black, it yields acetic acid:—

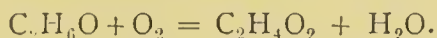
$$2\text{C}_2\text{H}_4\text{O} + \text{O}_2 = 2\text{C}_2\text{H}_4\text{O}_2.$$

But acetic acid, or vinegar, is made chiefly by the destructive distillation of wood (p. 25), or by oxidizing dilute solutions of alcohol by exposure to the air, under the influence of the vinegar plant (*Mycoderma aceti*). Vinegar can only be made by the acetous fermentation of dilute solutions of alcohol, such as claret, hock, and beer, for the ferment is killed by strong alcohol. Hence the stronger wines, such as port and sherry, are not apt to become sour like those which are lighter.

Vinegar has long been made in France by placing a little wine in a cask partly open to the air. Acetous fermentation soon commences, and the wine becomes covered with a thin coat of the vinegar plant; more wine is then added in small quantities at a time, until the vat contains about 200 litres of vinegar. About half this is withdrawn,

and the remainder constitutes what is technically known as 'a mother.' A little fresh wine is added to the 'mother,' and afterwards 10 litres of vinegar are removed and replaced by 10 litres of wine regularly once a week, as long as the cask works well.

In a more modern process, called the 'quick vinegar process,' wine or some other dilute spirituous liquor is made to flow slowly over beech-wood shavings, which have been moistened with vinegar in order that they may become coated with the vinegar plant. As the fluid trickles over the shavings it comes into contact with the organism in the presence of air, and its alcohol is oxidized :—

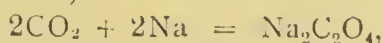


The superiority of the quick vinegar process is due to the circumstance that the liquid is much more freely exposed to the air as it flows in shallow streams over the shavings, than when it stands in a cask as in the French process.

Vinegar is not simply a solution of acetic acid. It also contains colouring matter, &c. Pure acetic acid is a colourless crystalline solid, which melts below 17° . It is slightly more dense than water, and has a sharp pungent odour. Its vapour is combustible. In solution it attacks some of the metals, and many of their oxides, forming salts called acetates, and the pure acid, which is corrosive to the skin, is often used as a solvent for organic compounds. It also dissolves such substances as iodine and sulphur.

The acetates are crystalline, soluble in water, and are readily decomposed by mineral acids. Some basic acetates, such as *verdigris*, are only partly soluble. Acetic acid may be recognized by its odour. When an acetate is warmed with a mixture of alcohol and strong sulphuric acid, a fragrant smelling compound, ethyl acetate, is formed.

Oxalic acid. This acid occurs in the juices of several plants, for example the sorrel, sometimes in the form of the acid salt, KHC_2O_4 , and also often as calcium oxalate. It is a white, crystalline, poisonous solid, acid to litmus. It is used for cleaning brass, &c. It is made on the large scale by heating sawdust with potash, KHO , and soda, NaHO , to about 250° , and dissolving out the salt produced with water and then liberating the acid. It can be formed by the action of carbon dioxide on sodium at 350° ,



and by the oxidation of various organic substances.

Experiment. Warm 25 grams of sugar in a large flask with 125 c.c. of strong nitric acid till red fumes (N_2O_4) are evolved freely, and then remove the source of heat. When the action ceases, allow the liquid to cool and drain the crystals which may have formed, or evaporate the liquid in a dish in a fume closet to obtain a larger supply. Finally, re-crystallize the crude acid from hot water. Other carbohydrates (p. 350) may be substituted for sugar.

Heat a little oxalic acid with strong sulphuric acid, and test the gases evolved for carbon monoxide and dioxide (see also p. 321).

Try the action of heat on the acid, first, at 100° , then at 160° , finally at a higher temperature. Notice whether it gives off water at 100° , sublimes at 160° , and decomposes at higher temperatures.

Warm some oxidizing agent, e.g. a solution of potassium permanganate with oxalic acid and a little sulphuric acid. Notice the change of colour which ensues. For the explanation, and for an application of this reaction, see p. 469, Exp. 301.

Prepare the neutral sodium salt of oxalic acid, and observe the behaviour of this with a solution of a soluble calcium salt. Prepare also some of the acid oxalate of potassium or sodium.

Tartaric acid. This acid occurs frequently in fruits such as the tamarind and the grape, sometimes as free acid, but very often as the acid salt $\text{KHC}_4\text{H}_4\text{O}_6$ (p. 406, see 365). It can be made also by oxidizing the sugar present in milk, and from cane sugar. But we obtain it chiefly from the 'tartar,' $\text{KHC}_4\text{H}_4\text{O}_6$, deposited by grape juice during fermentation. This latter salt exists in the grape juice; it is slightly soluble in water, but much less soluble in alcohol. Hence as the sugar of the grapes is converted into alcohol the 'tartar' is deposited.

Prepare a few cubic centimetres of a cold saturated solution of the salt known as 'cream of tartar,' $\text{KHC}_4\text{H}_4\text{O}_6$, add an equal volume of methylated spirit to it, and observe that crystals fall, note the crystalline form, action on litmus, &c., of the salt.

Heat a gram or two of the salt, $\text{KHC}_4\text{H}_4\text{O}_6$, in a dry test-tube, and observe the result. Notice how its behaviour differs from that of an oxalate, and ascertain whether there is any carbonate in the residue by warming the black carbonaceous matter with a little water, filtering, evaporating the solution thus obtained to dryness and testing what is left for a carbonate (p. 318); test also for potassium (p. 407).

Tartaric acid may be obtained in the free state by mixing a neutralized solution of cream of tartar with a neutral solution of

calcium chloride, collecting and washing the precipitate of calcium tartrate and decomposing it with an equivalent quantity of sulphuric acid. This converts the calcium of the salt into insoluble calcium sulphate and liberates the acid:—



If the product is filtered, and the filtrate cautiously evaporated, it will yield crystals of tartaric acid.

Further experiments. Mix some solution of tartaric acid with a solution of sodium bicarbonate, and observe the effect produced:—



Now mix dry, well-powdered tartaric acid with dry bicarbonate of soda. Observe the result.

Add water to the mixture. Notice that effervescence at once occurs.

The indifference of tartaric acid and soluble carbonates to each other in the dry state is made use of in various ways:—

Thus, *baking powder* consists of such a mixture diluted with flour or rice starch. When this is mixed with flour and afterwards moistened, the gas evolved (CO_2) forms minute bubbles or cavities in the dough, which are expanded afterwards by the heat of the oven, and thus a *light* porous bread is obtained without the use of yeast (see p. 342 b).

A somewhat similar result can be produced by using bicarbonate of soda alone. This evolves carbon dioxide if hot water is added to it or in an oven, and so has a similar power of ‘raising’ dough, whence the name *baking soda*.

Sherbet, also, consists of a mixture of a bicarbonate and tartaric acid, sweetened with sugar and flavoured with oil of lemon peel. And the effervescent quality of certain medicines, such as seidlitz powders, is secured in a similar way.

Citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$, H_2O , and malic acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_5$, are other important vegetable acids. The former occurs in the juice of lemons in considerable quantity, and can be prepared from this by a process analogous to that by which we make tartaric acid. Lemon juice owes its wholesome and refreshing qualities largely to this acid.

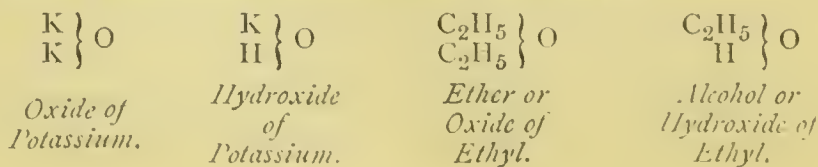
Malic acid is plentiful in the juice of apples, gooseberries, mountain ash, &c. It is soluble in water *and in alcohol*. Hence, when the juice of apples or gooseberries is fermented, the acid contained in it is *not*

thrown out of solution like the tartar of grape juice. This is the explanation of the acidity and generally inferior quality of the alcoholic beverages prepared from fruits, such as the gooseberry, which contain malic acid.

The above are only a few of the numerous acids derived from vegetable sources. Another interesting example is gallic acid, $C_7H_6O_5$, which is extracted from oak galls and also from the leaves of certain kinds of oak, from sumach, tea, and many other plants. It can be extracted from oak galls by exposing them when powdered and mixed with water to the air for a few weeks, when a fermentation ensues. After a while the gallic acid can be extracted by means of boiling water. Another substance derived from oak galls, tea, &c., is tannic acid or tannin, $C_{14}H_{10}O_9$. If oak galls are extracted with a mixture of ether and alcohol, we obtain a liquid which separates into two layers, the lower one consisting of water which holds the tannin in solution. When this solution is evaporated it deposits tannin as a porous mass. A solution of this substance in water precipitates white of egg and yields a compound with iron which forms the basis of ink. This may be obtained by adding a solution of a ferric salt to some solution of tannin, and the reaction may be used as a test for tannin or for ferric compounds. Its action on gelatine is made use of by the tanner. Add some solution of tannin to some liquid glue and notice the precipitate which falls. The process of tanning skins depends on this reaction. The skins to be tanned being soaked in a solution of oak bark or other substances containing tannin, when the latter is gradually absorbed by the gelatinous material of which the hides are composed, forming what is known to us as leather.

The same reaction may take place inside our bodies if we drink strong astringent tea after, or together with, a meat meal, when the conversion of part of the gelatine of the meat into a kind of leather is apt to produce indigestion.

300. Ether ($C_4H_{10}O$). When alcohol is suitably treated with sulphuric acid we obtain a highly interesting substance called *ether*. This compound is oxide of ethyl (C_2H_5)₂O; it is related to alcohol as oxide of potassium is related to the hydroxide:—



EXPERIMENT 236. To prepare ether from alcohol. Warm a mixture of one part of strong alcohol with two parts of strong sulphuric acid in a flask *A* (Fig. 107), provided with a condenser *B*, and a receiver

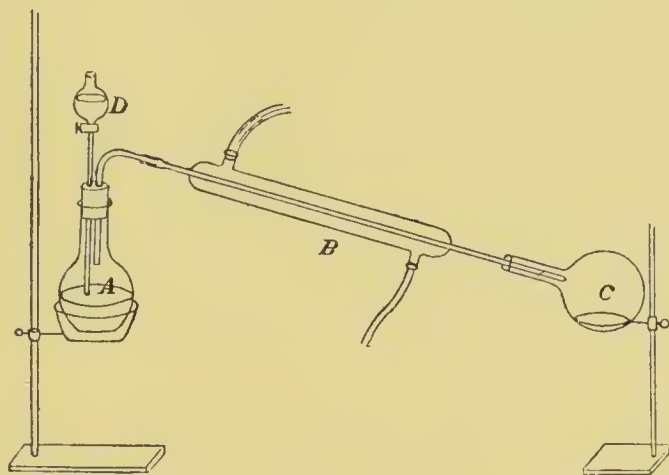
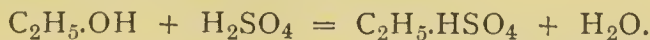


Fig. 107.

*C**, using a sand bath to protect the flask. When the temperature of the contents of *A* has risen to 140° , and the liquid has begun to boil, add more alcohol *slowly* from the reservoir *D*. A liquid will collect in *C*, which will consist of ether floating above alcohol and water. The latter will probably have sulphur dioxide in solution. Pour the contents of *C* into a separating-funnel, such as *D*, add a little potash, shake well, draw off the watery liquid, and dry the ether by shaking it with a few fragments of calcium chloride. It may be purified by redistilling it from a water bath if a sufficiently large quantity has been secured.

Ether is a colourless liquid with a peculiar, yet agreeable, odour. Its formation is understood to take place at two stages. First, ethyl hydrogen sulphate ($\text{C}_2\text{H}_5\text{HSO}_4$) † is formed :—



Secondly, this compound interacts with more alcohol producing ether and sulphuric acid :—



Thus the alcohol is resolved into ether and water, and the acid

* As ether is highly inflammable the experiment should be supervised closely by a teacher, if it be performed by a young student.

† Compare KHSO_4 .

remains unaltered. Theoretically a given supply of sulphuric acid should convert an unlimited amount of alcohol into ether, and a small quantity of the acid does, in fact, act upon a relatively large quantity of alcohol, but its powers are not unlimited, partly because it is gradually reduced to sulphur dioxide, and partly because some of the water formed remains in *A* and dilutes the acid.

EXPERIMENT 237. **Some properties of ether.** 1. Shake up a little ether with some water, then remove the water by means of a separator and smell it. It will be found to have acquired a strong odour of ether, as the latter is soluble in about ten times its volume of water.

2. Place a little ether in a gas cylinder, cover its mouth with a ground-glass plate, shake the cylinder well, remove the glass plate, and bring a light to the mouth of the cylinder. The ether will at once catch fire ; possibly an explosion may occur.

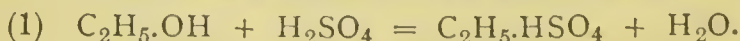
3. Pour a little ether into the palm of your hand. It will evaporate rapidly, producing in a marked degree the sensation of coldness. A fine spray of ether is often used in the minor operations of surgery.

4. Shake fragments of iodine and sulphur with ether, then evaporate a few drops of the ether on a clean surface. You will find that both sulphur and iodine are more or less soluble. Treat a little fat and resin in the same way. These also will dissolve.

Ether boils at 35° . Its great volatility and inflammability make it, like carbon disulphide, a somewhat dangerous substance, and it should be preserved in well-closed bottles, and kept away from flames. When ether is inhaled it causes insensibility, hence it is sometimes used as an anæsthetic.

301. Ethylene, olefiant gas (C_2H_4). This gas is one of the products of distilling wood and coal, and is formed in many chemical changes.

EXPERIMENT 238. **To prepare ethylene.** Mix 8 parts of strong sulphuric acid with 1 part of strong alcohol, pour the mixture into a capacious flask half-filled with broken glass, and provided with a delivery tube, and apply heat till a gas is evolved. Wash this gas with alkali, to remove sulphur dioxide, and collect it over water or mercury. The following equations may explain the change* :—



Or



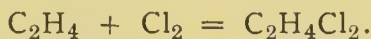
* Compare these changes with those which occur in the making of ether.

A more economical process consists in passing the vapour of alcohol through a mixture of 10 parts of oil of vitriol and 3 parts of water heated to 160° – 165° (Newth).

EXPERIMENT 239. Some properties of ethylene. Ethylene is a colourless, not very soluble gas, and possesses a sweetish taste. If a light be brought to a jar of it, it burns with a bright luminous flame. Under great pressure it can be condensed to a colourless liquid.

Chemically, ethylene (and its homologues) differs very distinctly from methane and the paraffins, for it readily unites with such substances as chlorine, bromine, fuming sulphuric acid, and hydriodic acid.

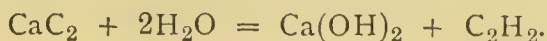
1. Pass moist chlorine and ethylene simultaneously into a large glass flask. Notice that an oily liquid condenses in the flask. This is *ethylene dichloride* ($\text{C}_2\text{H}_4\text{Cl}_2$), or *Dutch liquid** :—



2. Collect a little ethylene in a tube over mercury, and add some fuming sulphuric acid by means of a pipette. The ethylene will be absorbed readily. When ordinary sulphuric acid is used, the action is less rapid. Since a molecule of ethylene can combine with two atoms of chlorine or hydrogen and also with sulphuric acid, the combining powers of its constituent atoms must be partly unsatisfied. It is therefore said to be an unsaturated compound.

302. Acetylene (C_2H_2). This hydrocarbon, as we have previously learnt, is frequently produced in incomplete combustion. It is also produced by the direct combination of carbon and hydrogen when an electric discharge takes place between carbon poles in an atmosphere of hydrogen. But it is most conveniently prepared from calcium carbide.

EXPERIMENT 240. To prepare acetylene from calcium carbide†. Place some fragments of calcium carbide (CaC_2) in a small flask provided with a delivery tube and with a separating-funnel (see *A* and *D*, Fig. 107). Place some water in the latter and allow it to drop slowly upon the carbide. The following reaction will occur :—



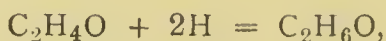
Acetylene is not quite insoluble, but it may be collected over water.

* Discovered by four Dutch chemists, 1795. Hence this name.

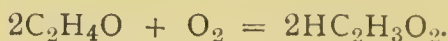
† Calcium carbide is formed when lime (CaO) is heated with carbon in an electric furnace.

It has a peculiar odour, which is sometimes compared to that of garlic *. It burns with a smoky, highly luminous flame.

The last method of making acetylene is of considerable interest; because both calcium carbide and water can be made from their elements, and because many other organic substances can be prepared from acetylene. Thus, if acetylene be dissolved in sulphuric acid, and if the product be diluted and distilled, aldehyde (C_2H_4O) is formed, and this can be converted into alcohol by the action of nascent hydrogen :—



and into acetic acid by exposure to the air :—



Finally, if acetylene be passed through a tube heated to dull redness, it will yield, among other things, a very important hydrocarbon called benzene (C_6H_6).

EXPERIMENT 241. Some properties of acetylene†. Pass a stream of acetylene through some solution of cuprous chloride containing excess of ammonia. A brownish-red precipitate will fall. This substance is called copper acetylene, or cuprous acetylide; it is believed to have the composition $C_2H_2Cu_2O$.

A little of the substance may be collected and dried.

1. Strike a small fragment of copper acetylene on an anvil. It will explode.

2. Heat some on the end of a knife. It will explode.

3. Pour some strong solution of hydrochloric acid upon the solid. Acetylene will be given off.

The production of copper acetylene affords a useful and delicate test for acetylene.

If silver nitrate be substituted for the copper salt in the above experiment, a still more unstable compound, silver acetylene ($C_2H_2Ag_2O$), is formed. And if the gas is passed over hot metallic sodium, part of its hydrogen is replaced by sodium, a compound having the formula C_2HNa being formed.

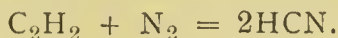
If a slow stream of acetylene escaping from a small gas-holder

* If the carbide contains any phosphide, phosphuretted hydrogen will be present in the gas.

† These experiments should be done by the teacher.

by a glass jet be brought near a flame, it will ignite, the acetylene burning with a luminous smoky flame.

When a mixture of acetylene and nitrogen is submitted to electric discharge it is said to form hydrocyanic acid (HCN):—



From the readiness with which acetylene enters into combination with other substances we suppose it to be an unsaturated compound.

303. Coal gas. When coal undergoes destructive distillation, it yields a residue of impure carbon, known as coke, and a variety of volatile products which may be divided roughly into (*a*) a mixture of gases which will burn with a luminous flame, (*b*) an ammoniacal watery liquid, and (*c*) tarry matter.

EXPERIMENT 242. To obtain the products of distilling coal. Pack a hard glass tube loosely with small fragments of bituminous coal; attach a small flask or U tube to one end of it, and close the other end (see Fig. 101). Then heat the tube, as in the making of charcoal from wood. A gas which burns with a luminous smoky flame, and which possesses an unpleasant odour, will escape from the coal, and a watery liquid possessing a faint odour of ammonia, together with tarry matter, will condense in the flask.

The gas is crude coal gas. The watery liquid is one of our chief sources of ammonia, and the tarry matter yields a great variety of valuable substances. It will therefore be worth while to enter rather more fully into the very important industry of gas-making.

In order to make coal gas, bituminous coal is heated strongly in retorts, *A* (Fig. 108). A number of these retorts are connected with the

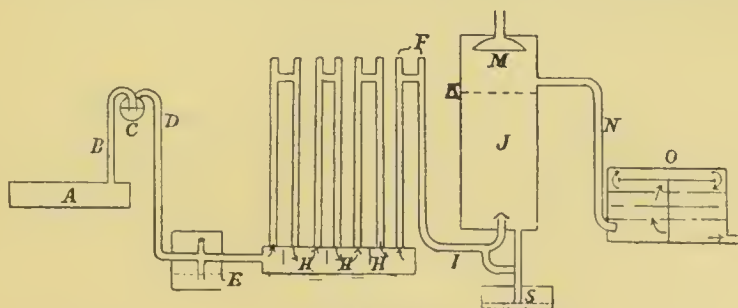


Fig. 108.

rest of the plant by means of tubes, *B*, and a long horizontal cylinder shown in section at *C*. Water in *C* prevents the gas in the rest

of the apparatus from returning to *A*, and thus escaping, when the retorts are opened to replace the coke with fresh coal. From *C* the gas passes, by *D*, through a pit *E*, in which much of the tar is deposited, and thence through a series of pipes *F*, in which it is further cooled, and deposits more tar, which falls into *H*. During the passage of the gas through *D*, *E* and *F*, a good deal of ammonia condenses together with water, and the ammoniacal liquor so formed is used for preparing sal-ammoniac. From the refrigerators *F*, the gas is conducted by *I* to a tower, or scrubber, *J*, where it is exposed to water supplied from above by *M*, which removes the remaining ammonia and falls into *S*. When it passes from *J*, the gas contains carbon dioxide and small quantities of hydrogen sulphide and carbon disulphide. It is therefore conveyed by *N* to the purifier *O*, in which it passes slowly over trays of slaked lime *. This absorbs carbon dioxide and most of the sulphur compounds, but does not remove all the carbon disulphide (for the use of the product see 205). Finally the gas is collected over water in a gas-holder, and thence distributed to the consumers.

The composition of coal gas depends partly on the coal it is made from, partly, also, on the details of its manufacture. The following table will give a general idea of the nature of its components:—

CONSTITUENTS OF COAL GAS.

Hydrogen	40 to 50 per cent.
Marsh gas	35 „ 40 „
Carbonic oxide	5 „ 6 „
Hydrocarbons, such as ethylene (C_2H_4), acetylene (C_2H_2), benzene (C_6H_6), &c. .	about 5 „
Nitrogen, chiefly the result of leakage .	2.5 to 5 „
Oxygen, carbon dioxide, carbon disulphide, &c.	

It will be seen that coal gas is chiefly composed of the two light gases, hydrogen and marsh gas; these, and also the carbon monoxide, burn with non-luminous flames, and therefore we must attribute its light-giving powers to the presence of the small percentage

* Ferric oxide is sometimes used in the purifier. The action which then occurs is as follows:—



The oxide can be reoxidized, by exposing it to air, and used again. When it is fully charged with sulphur the latter is recovered by distillation.

of hydrocarbons which are rich in carbon. The following experiment shows that the addition of such compounds as these to a gas like hydrogen bestows on the latter the power of producing a luminous flame.

EXPERIMENT 243. To render a hydrogen flame luminous. Fit at the two ends *A* and *B* of a Y-shaped tube (Fig. 109) two jets made of hard glass. Place a loose plug of cotton-wool *C* soaked with benzene in one arm of the tube. Connect *D* to a bottle in which hydrogen is being generated. Apply a light to the gas at *A* and *B*. The hydrogen impregnated with benzene will burn with a bright luminous flame, that which is free from benzene with a non-luminous flame.

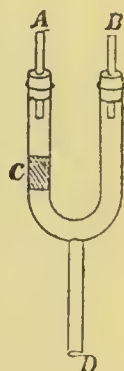


Fig. 109.

We may therefore divide the constituents of coal gas into the following three classes:—

- | | |
|--|--|
| I. Non-illuminating, heat-giving gases | { Hydrogen, marsh gas, carbon monoxide. |
| II. Illuminating gases rich in carbon | { Ethylene (C_2H_4), acetylene (C_2H_2), benzene (C_6H_6), &c. |
| III. Impurities | { Carbon dioxide, nitrogen, traces of oxygen and carbon disulphide. |

Oil gas. A useful illuminating gas may be made by dropping oil into a red-hot retort filled with coke. It is chiefly used for increasing the illuminating power of coal gas. If the use of the incandescent gas burner—in which an incombustible mantle, ignited by gas burnt in a Bunsen burner, serves as the source of light—should become general, the illuminating power of gas will be less important than it is at present; in which case coal gas is not unlikely to be replaced by less expensive substitutes, such as the water gas described in Expt. 219, 4.

Producer gas. This is used industrially as a source of heat. It consists of carbon monoxide and nitrogen, and is made by admitting a limited quantity of air into a chamber containing hot coke. Like 'water gas,' it burns with a clean non-luminous flame.

304. The chemistry of a coal fire. The student will now understand that the changes which occur in a coal fire do not consist solely in the oxidation of the coal. When fresh coal is thrown upon a mass of glowing carbon it decomposes, and gives off combustible

gases and tarry matters much as it does when heated in a retort. The distillate consists chiefly of compounds of carbon and hydrogen, and burns, as we see every winter's day, giving tongues of more or less smoky and luminous flame, and producing ultimately water and carbon dioxide, together with unburnt carbon (smoke). After a time a mass resembling coke is left, which consists chiefly of carbon. If the fire burns well this mass is red-hot, and is crowned with a non-luminous blue flame like that of carbon monoxide. At this latter stage the chief ultimate product of the combustion is carbon dioxide mixed, perhaps, with some carbon monoxide, sulphur dioxide, and a little water produced by the combustion of any hydrogen left in the coke.

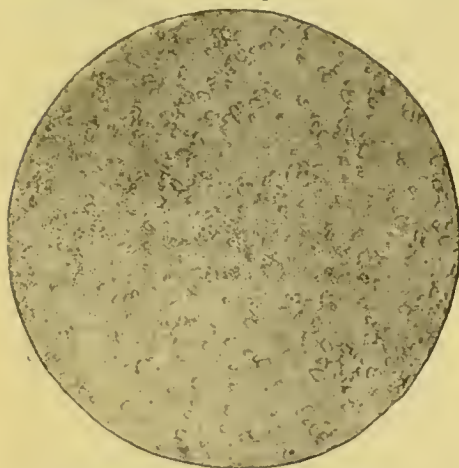
305. The carbohydrates. Besides the comparatively simple substances mentioned in the previous pages, there are many other interesting and important compounds of carbon, such as benzene (C_6H_6), a very volatile liquid extracted from coal tar, which is a most useful solvent, and from which aniline and the aniline dyes are made, and the alkaloids and other substances used in medicine and the arts. Still more important are the so-called 'carbohydrates,' which are composed of carbon, hydrogen, and oxygen, the two latter elements being present in the proportions in which they form water; these are plentiful in the tissues and juices of plants. The chief carbohydrates which can be mentioned here are—

Cellulose ($C_6H_{10}O_5$)_n, or ($C_{12}H_{20}O_{10}$)_n. This is the chief constituent of wood, cotton, linen, and of those parts of plants which compose their framework, and is the chief component of paper. It may be obtained from linen, hemp, or cotton-wool, if their mineral matter be removed. Cellulose is insoluble in ordinary solvents, but it is gradually destroyed by the action of acids. Thus, if it be treated with strong sulphuric acid, it gradually dissolves, and if the solution thus obtained be diluted and boiled, the cellulose is changed into dextrin, and finally into a fermentable sugar. A mixture of nitric and sulphuric acids converts cellulose into the explosive, gun-cotton (229).

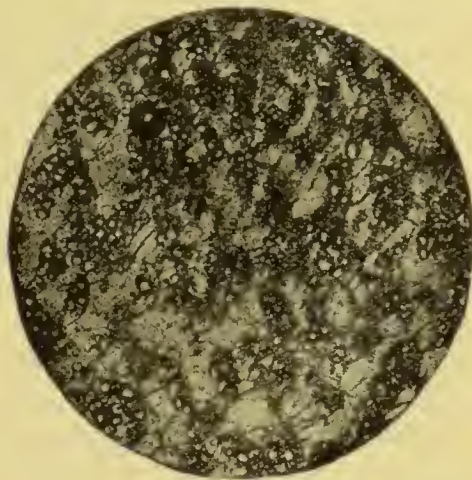
Starch ($C_6H_{10}O_5$)_n occurs largely in vegetables, and forms an important constituent of such food-stuffs as wheaten flour, potato, arrowroot, tapioca, sago, and rice. In wheaten flour it is accompanied by a valuable nitrogenous food-stuff called *gluten*.

Starch may be extracted easily from potatoes by crushing them, mixing them well with water, decanting the milky liquid from the fibres, and allowing it to stand. When this is done a sediment of

starch granules soon subsides, and a small portion can be examined under the microscope.



STARCH FROM ARROWROOT.



SLICE OF POTATO SHOWING
CELLS AND STARCH GRANULES.

Starch is converted into dextrin when heated for some time to 210° , and, as we have previously learnt, a fermentable sugar called maltose is produced when a solution of starch is warmed with malt to 65° (298). Starch may be recognized by means of iodine (see 165, 6).

The sugars. Grape sugar ($C_6H_{12}O_6$) and cane sugar ($C_{12}H_{22}O_{11}$) are other important carbohydrates. The former occurs in many fruits, such as the grape, and it is one of the constituents of honey. The latter is obtained from the sugar-cane and from beetroots.

306. The proteids and other food-stuffs (see also 77, 78). If we had time to study our various food-stuffs in detail, we should learn that a few components predominate, though they are present in varying proportions. These components are (1) fat ; (2) the carbohydrates ; and (3) such substances as white of egg, gluten, and muscular fibre, or flesh. The latter substances are examples of what are called *proteids**. The proteids, which are numerous, all contain carbon, hydrogen, and oxygen, together with nitrogen and a little sulphur and phosphorus, and they form an essential part of our food. Although our bodies are largely composed of proteids, it would seem that we cannot elaborate such substances for ourselves from inorganic materials ; but the plants can do this ; and they prepare the food-stuffs of the herbivora, which, in their turn, supply the carnivora.

* For further information on these highly interesting compounds, the student should consult an elementary work on physiology.

In order that our bodies may be fully nourished the following substances must be supplied by our food, viz. proteids, starch or sugar, fat, certain mineral substances, such as salt and the mineral components of the bone, and water. It is impossible for us to live on carbohydrates and water alone, or even on carbohydrates with water and mineral matter, for we must have nitrogen and sulphur, and these can only be obtained in a suitable state in the form of proteids. No one could live long on a diet composed of starch, sugar, mineral matter, fat, and water, for none of these substances contain nitrogen or sulphur. We could, it is true, exist on proteid foods, such as flesh and eggs or cheese, with the addition of a few minerals, for these afford all the necessary elements for restoring every part of our bodies; but such a diet would not be economical, nor wholesome, for man has become accustomed to consume a more mixed diet.

It has been calculated that on an average the necessary daily food of an adult human being should consist of:—

Proteids in the form of flesh, &c.		115 grams
Fat		60 „
Starch, &c.		500 „
Salt		30 „
Water		2800 „

But no single article of food affords this combination*.

Sugar and minerals alone, of all the above food-stuffs, are soluble and also able to pass through the membranes of which our bodies are composed. If you place white of egg, starch paste diluted with water, or some oil in the apparatus employed for Experiment 245, and subsequently examine the water in the outer vessel, you will find that none of them pass through the parchment, though sugar will do so. Similarly, if they were placed, unaltered, in the alimentary canal they would never pass through the membrane of which it is composed, and would never reach the various organs which they are to nourish, were it not that these colloidal substances become modified in the stomach, by various secretions, during the processes of digestion. In these processes the starch, partly under the influence of the saliva, is converted into sugar, which is a diffusible substance (see 309); the proteids are gradually dissolved, yielding solutions which easily pass through the membranes of the intestines

* Bread, which contains both carbohydrates, proteids, and mineral matter, would sustain life, if necessary, comparatively well, for the proteids need not be of animal origin.

and so into the blood; and the fat is converted into an emulsion, in which it is so finely divided, that it can be absorbed by certain organs, and by them be transferred to the blood to rejoin the other constituents of the food, and be carried with them to all parts of our bodies. Sooner or later all these food-stuffs undergo oxidation, and when their work is done their components are expelled from the organism in the form of certain simple compounds, the hydrogen chiefly as water, the carbon mainly as carbon dioxide, the nitrogen as urea (289), and the sulphur and phosphorus as sulphates and phosphates.

SILICON (Si): Atomic weight, 28.2.

This element does not occur free in nature, but is found in silica (SiO_2), and in the silicates, which are numerous.

307. Silica. The most familiar forms of silica are sand, flint, and quartz or rock crystal, whilst opal and jasper are more highly prized varieties of the same substance.

EXPERIMENT 244. To prepare silica. Pure silica may be prepared from sand or flints, or from mineral silicates, in the following manner. Heat the powdered raw material* with three or four times its weight of dry carbonate of soda, or of a mixture of the carbonates of soda and potash in molecular proportions, in an iron ladle till it fuses, and until all effervescence has ceased. Allow the fused substance to cool, treat it with hot water to extract the soluble alkaline silicate, add excess of strong hydrochloric acid to the solution, and evaporate the mixture to dryness. Finally, boil down the residue with strong hydrochloric acid several times, remove the sodium chloride, thus formed, by washing with water, collect the silica which remains on a filter and dry it.

In this process the silica (SiO_2) replaces the carbon dioxide of the carbonate, forming a sort of soluble glass, *sodium silicate* (Na_2SiO_3), which is afterwards decomposed as suggested by the following equation:—



Some properties of silica. Pure silica is a colourless, insoluble solid, which occurs as quartz or rock crystal in the form of hexagonal prisms terminated by pyramidal summits (339, VI). Its density in

* To powder a flint, heat it to redness, and drop it quickly into cold water. You will then be able to rub it into a powder in a mortar.

this form is 2.6. It is sometimes tinted, as in the case of amethystine quartz, which owes its colour to the presence of traces of oxide of manganese. In the amorphous form silica is met with in the opal; and agate, flint, and chalcedony are mixtures of the crystalline and amorphous varieties. The gelatinous precipitate which is formed when an acid is added to a solution of an alkaline silicate contains water ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), and yields the anhydrous oxide in the form of a white powder when it is ignited. When silica is heated in the oxyhydrogen flame it becomes viscous; it can then be drawn into extremely fine threads, which conduct electricity very badly, and are useful to the physicist, and can be fashioned into tubes of various forms which are occasionally useful to the chemist.

Chemically, silica must be ranked among the acidic oxides, for it combines with strong bases, such as potash and soda, and liberates carbon dioxide from alkaline carbonates, yielding salts known as *silicates*.

The commoner solvents, such as sulphuric acid, nitric acid, and hydrochloric acid, are without action on silica, but it dissolves in fused alkalis, and both silica and its compounds are readily attacked by hydrofluoric acid (175). Owing to the solubility of silica in solutions of alkaline carbonates, it exists in small quantities in nearly all natural waters, and the hot springs (geysers) which rise near volcanoes are often highly charged with silica, which is deposited as the water cools.

The molecular weight of silica is unknown.

308. Silicic acid. This acid may exist in the solution of silica which is prepared by a process to be subsequently described, but the pure acid is unknown. From the composition of various silicates it may be supposed that *orthosilicic acid* would correspond to the formula H_4SiO_4 , and that by loss of water this may give rise to other hydrates such as:—



309. Dialysis. This name has been given to a process which is often employed for separating colloidal from crystalline substances. It is based on the fact that whilst the former are incapable of passing through a wet membrane, such as parchment, the latter readily do so.

EXPERIMENT 245. To separate colloid silica from crystalline substances by dialysis. Make a dialyzer (*A*, Fig. 110) by cutting off the upper part of a wide-mouthed bottle, and, after removing the

sharp edges with a file, tying a sheet of wet parchment or parchment paper securely over its end. Add a little hydrochloric acid to a rather weak solution of starch, place some of the mixture in the dialyzer, and suspend the latter in a vessel of water as shown in the diagram. After a while test the contents of the outer vessel for hydrochloric acid and for starch. You will find that the former alone has passed through the wet parchment; and similar results will be obtained if other solutions containing mixtures of colloids with crystalline substances are experimented with. Thus, for example, to obtain a solution of silica, add some dilute solution of sodium silicate to some dilute hydrochloric acid, taking care that no silica is precipitated. Place the mixture in the dialyzer *A* (Fig. 110). Change the water in *B* from time to time, for as soon as the proportions of salt and free acid in the solutions on the opposite sides of the membrane become equal the progress of the experiment is arrested, and continue the process till no more acid enters *B*.

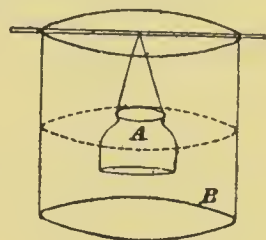


Fig. 110.

When the contents of the dialyzer are free from acid and salt, they may be concentrated by cautious evaporation. If the solution be evaporated *in vacuo* it leaves a jelly which is said to correspond to the formula H_2SiO_3 .

310. The silicates. The silicates form an exceedingly numerous and important class of compounds, and they constitute a very large part of the earth's crust. The following are a few of the more important of them:—

Felspar. A silicate of potassium and aluminium, $\text{K}_2\text{Al}_2\text{O}_4(\text{SiO}_2)_6$, which occurs alone, and also mixed with mica and quartz in granite.

*Clay**. A more or less impure hydrated silicate of aluminium. It is formed by the decomposition of felspar, and is valuable on account of its power of forming a plastic mass with water which hardens when baked. *Kaolin*, or 'potter's clay,' which is found in large quantities in Cornwall, is a nearly colourless clay, to which the formula $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$ may be given. The porous pots used for galvanic cells are made of baked clay, and the commoner qualities of table ware are made of the same substance glazed superficially with a coating of a fusible silicate. The latter may be applied by throwing

* Clay which contains calcium carbonate is called *marl*.

common salt into the furnace in which the ware is fired. The better varieties of earthenware are glazed by dipping the articles, after a preliminary firing, in water which holds in suspension a suitable substance *, or mixture of substances, in a fine state of division. The solid particles are carried to the surface of the porous material by the water which it absorbs, and form a coating, which is converted into a fusible silicate by means of a subsequent firing, and spreads itself over the entire surface of the material.

Stoneware is a coarse variety of porcelain made from clay containing oxides which cause it to be partially fusible. It is usually glazed by throwing salt into the furnace.

Porcelain. True porcelain may be distinguished from earthenware by its translucency and compactness, and by the smooth appearance of its surface when it is fractured. It is made from mixtures of the finest china clay with some fusible substance, such as felspar; the latter melts during the firing, is absorbed by the infusible clay, and binds the whole into a mass which becomes solid on cooling.

Other interesting silicates are *mica*, which occurs in granite; *hornblende*, *serpentine*, *meerschaum*, *talc*, *asbestos*, and *steatite*, which are silicates of magnesium; and *basalt*, *porphyry*, and *trap-rock*, which are mixtures of felspar with other compounds containing silica.

311. Glass. We have learnt how the silicates, clay, and felspar, are made use of by the makers of earthenware and porcelain. Silica is used by makers of mortar and cements, and large quantities are employed in the manufacture of glass, which is a mixture of fusible silicates. Flint, or English glass, is made by fusing together purified sand, red oxide of lead, and sulphate, or carbonate, of potassium. It is costly to produce, but is distinguished by its ready fusibility, high density, and fine lustre. The common, soft-glass tubes, which we use in the laboratory, contain no oxide of lead, but a good deal of soda; and the 'hard glass' of Bohemia, which is so difficult to melt, contains a large proportion of silica, together with lime, oxide of potassium, and smaller quantities of other constituents. Thus glass and porcelain are both composed of silicates, but whilst the former consists of materials which are entirely fusible, the latter consists largely of infusible components. Hence the transparency of the one and the comparative opacity of the other.

* Lead oxide and lead silicate are among the substances used.

The colours of some kinds of glass are due to the addition of certain oxides. Thus wine bottles owe their colour to ferrous oxide, blue glass often contains cobalt, some red glass contains cuprous compounds; chromium oxide gives a green glass, and a peculiar yellow glass is obtained by means of uranium.

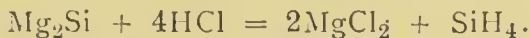
312. Elementary silicon. Although silica is so common, elementary silicon has not been found in nature. A little may be prepared from silica by igniting it with several times its weight of magnesium in powder, and treating the product with acid, to remove magnesia and excess of magnesium. It is then left as a dark-brown amorphous powder.

Silicon combines with fluorine and, in a less degree, with oxygen, sulphur, chlorine, and bromine. If it be strongly heated it becomes darker, more dense, and comparatively inert. It can be obtained in crystals by passing the vapour of silicon chloride over molten aluminium, when the following change occurs:—



The silica thus formed remains in solution in the excess of aluminium, which may be dissolved away afterwards by an acid. Another method of isolating silicon consists in reducing potassium silicofluoride (K_2SiF_6) with sodium and zinc. The materials, previously mixed, are fused together, and the product is treated, when cold, with acid to dissolve the zinc. The silicon then remains in long needles. Silicon is met with in a graphitic form which conducts electricity. It can be melted and even boiled in the 'electric arc.'

313. Silicon hydrides. Like carbon, to which it is nearly related (see table on p. 181), silicon forms a tetrahydride (SiH_4). This may be obtained, mixed with hydrogen, by heating silica with magnesium, and treating the impure magnesium silicide with an acid:—



Pure silico-methane (SiH_4) is even more inflammable than marsh gas. When burnt it produces water, and a white smoke consisting of silica. It burns spontaneously in chlorine, and is converted into silicon and hydrogen if it is passed through a red-hot tube.

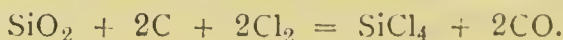
When silicon is heated with hydrochloric acid it yields a compound analogous to chloroform in composition, which is called *silico-chloroform* (SiHCl_3).

314. Silicon nitrides. When silicon is heated strongly in

nitrogen a white infusible nitride is formed. It is only soluble in hydrofluoric acid, but when acted on by water and carbon dioxide it yields ammonium carbonate.

315. Silicon carbide (SiC) (carborundum) is an extremely hard substance which is insoluble in all acids. It is made by heating together carbon and sand to an intense temperature.

316. Silicon chloride (SiCl_4). This substance can be produced by the direct combination of its constituents; but it is more conveniently made by heating a very intimate mixture of carbon and silica to redness in dried chlorine. The silica and carbon should be placed in a porcelain tube provided with an efficient condenser:—



Silicon tetrachloride is a volatile liquid which, like many other non-metallic chlorides, is readily decomposed by water:—



There is also a hexachloride of silicon (Si_2Cl_6), and a tetrabromide and an iodide are known.

Silicon tetrafluoride (SiF_4): see 175.

A further account of the members of Group IV will be found in Chapter XXIX, p. 433.

CHAPTER XIX

BORON (B): Atomic weight, 10.9.

317. THIS element, which does not occur free in nature, is obtained by reducing boric oxide (B_2O_3) with magnesium, and washing the product cautiously with dilute hydrochloric acid, alcohol, potash, and water. When prepared in this way it forms a dark amorphous powder, which burns in air or oxygen and is attacked by nitric acid, fused caustic alkalis, and chlorine. Boron forms a gaseous hydride (BH_3), which burns with a green flame. This may be obtained, mixed with hydrogen, by heating together magnesium and boron trioxide, and treating the product, which probably contains magnesium boride, with hydrochloric acid, but it has not yet been obtained in the pure state.

Compounds of boron with chlorine (BCl_3), bromine (BBr_3), and fluorine (BF_3), have been prepared. The two former are volatile

* The silica is precipitated in the gelatinous, hydrated form.

liquids made by the action of chlorine and bromine respectively on a strongly heated mixture of boric oxide and carbon; the latter is a gas made by heating a mixture of fluorspar, dry borax, and strong sulphuric acid. These compounds are decomposed by water.

318. Boric acid and borax. Boric acid ($B(HO)_3$ or H_3BO_3) occurs in the waters of certain hot lagoons in Tuscany. A borate of sodium (tincal) occurs in certain lake basins in several parts of Asia and in the United States, and calcium borate is also found in considerable quantities. Boric acid is easily prepared in the crystalline form by adding 1 part of sulphuric acid to 3 of borax dissolved in boiling water, and allowing the solution to cool. The acid is a moderately soluble substance. Its solution possesses but little taste, and imparts a wine-red colour to blue litmus. Its soluble salts are alkaline to litmus. When the solid acid is strongly heated it loses water, yielding a glassy mass which dissolves many of the metallic oxides.

Boron forms a series of acids analogous to those of phosphorus. Thus metaboric acid (HBO_2) and pyroboric acid ($H_2B_4O_7$) may be obtained by the action of heat on the orthoacid (H_3BO_3).

Borax. This has the formula $Na_2B_4O_7, 10H_2O$. It is a colourless salt with an alkaline reaction to litmus. When strongly heated it parts with its water of crystallization, leaving a glassy residue. If metallic oxides be heated with this residue they dissolve, and, in many cases, communicate characteristic colours to it. It is thus useful to the analyst.

Borax is generally regarded as a compound of sodium metaborate ($NaBO_2$), boric anhydride (B_2O_3), and water ($2NaBO_2, B_2O_3, 10H_2O$), but it may be a salt of pyroboric acid ($Na_2B_4O_7, 10H_2O$).

Compounds of boron communicate a green tinge to non-luminous flames when suitably treated. For example, if borax be moistened with spirit of wine and then acidulated with strong sulphuric acid, the spirit will burn with a green flame.

PART IV

THE RELATION OF HEAT AND ELECTRICITY TO
CHEMICAL CHANGE. THE SPECTROSCOPE
AND CRYSTALLOGRAPHY

CHAPTER XX

CHEMICAL AFFINITY. HEAT AND CHEMICAL ACTION.
ELECTROLYSIS AND SOLUTIONS

319. Chemical affinity. The hypothesis that chemical compounds are formed by the union of minute particles called atoms (see p. 101) has long been accepted by most chemists, but we cannot say why these atoms unite, or why a given kind of atom, say an atom of oxygen, combines readily with atoms of the metals, but less readily with those of chlorine, and, apparently, not at all with atoms of fluorine.

The term chemical affinity is applied to that property, whatever it may be, which causes atoms to combine, and which enables molecules to interact, and produce new combinations by the rearrangement of their constituent atoms.

Many facts show that chemical affinity does not act equally well under all circumstances. For example, it does not act between atoms which are at a distance, for it is necessary to bring two substances into contact before chemical action can take place between them.

Again, chemical affinity acts selectively, and when two or more atoms are united their attractive power for other atoms seems to be diminished (see 137 and 106).

The action of chemical affinity may be overcome by heat and electricity, as we have seen in a number of instances, and yet energy from outside sources must sometimes be supplied before the parts of a given system of atoms can interact (see 327).

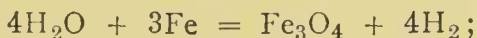
When we seek to trace the influence of affinity in the case of any given chemical change, we at once meet with difficulties owing to the fact that the behaviour of a given set of atoms does not depend on their affinities alone.

The following illustrations will make this clear :—

From Experiment 53 we learnt that when hydrogen is passed over heated oxide of iron the latter is reduced :—

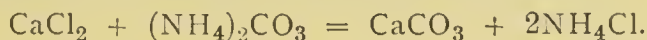


May we conclude from this that oxygen has more affinity for hydrogen than for iron? We might be inclined to do so if we had not learnt from another experiment (52) that when steam is passed over red-hot iron hydrogen is liberated and iron oxide formed :—

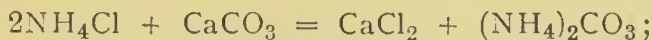


which suggests that iron, and not hydrogen, possesses the greater affinity for oxygen. As a matter of fact, in the first experiment we used a large excess of hydrogen, and in the second a large excess of steam, which makes it impossible to draw any just conclusion as to the relative affinities of iron and hydrogen for oxygen from the result of either experiment.

Again, in order to detect calcium in a salt of that metal we may add to its solution some solution of ammonium carbonate. When we do so a precipitate of calcium carbonate (CaCO_3) falls :—



We might consider this change to be due to the superior affinity between calcium and the group CO_3 , were it not that ammonium carbonate can be made by heating a mixture of chalk and sal-ammoniac, when the first change is reversed and ammonium carbonate sublimes :—



from which it is clear that the insolubility of the carbonate of calcium, and the volatility of the ammonium carbonate, greatly influence the results of the two experiments.

Berthollet long ago suggested that substances which combine chemically, act by reason of their affinities, and of the masses in which they are presented to one another *. If this statement be accepted,

* Berthollet's law has been developed during recent years by Guldberg and Waage, but further details must be sought in one of the larger treatises, or in a work on physical chemistry.

it becomes evident that reactions in which solids or gases are generated from solutions must not be selected if we wish to study the relative affinities of atoms, for the substances concerned in such reactions are not equally free to act, since some of them quickly pass from the sphere of action in the gaseous or solid state. Therefore if we wish to investigate the relative affinities of a given set of elements or radicles, we must study changes which are not complicated by physical differences among the substances concerned, and further we must bring together these substances in suitable and carefully regulated quantities. Unfortunately, these conditions are often difficult to fulfil, and, moreover, it is difficult to measure the respective masses of the constituents of mixtures of gases or liquids, except by indirect means, such as those which are briefly alluded to at the close of the following section.

320. Strong and weak acids. Affinity constants. If excess of sulphuric acid and common salt are warmed together, hydrochloric acid is freely evolved until the salt is entirely decomposed; and sulphuric acid will similarly decompose other chlorides and also nitrates. These and similar reactions are much used in preparing free acids and in chemical analysis, and they have led chemists to think of sulphuric acid as a *strong acid*, able to withdraw the metals from the salts of many other acids. We might be inclined to accept this conception concerning sulphuric acid if we did not remember that hydrogen chloride is a gas, and nitric acid a very volatile liquid, and that in the changes in question they are removed from the scene of action almost as quickly as they are produced, and thus prevented from reacting with the sodium sulphate which is formed at the same time, as otherwise they conceivably might do. Accordingly we ought not to be surprised to learn that there is considerable reason to believe that, when one equivalent each of nitric acid (HNO_3), sulphuric acid ($\frac{1}{2}\text{H}_2\text{SO}_4$), and potash (KHO) are mixed in the same solution, the proportions of the potash which act with the two acids respectively are approximately in the ratio 10:7; from which it would appear that the tendency of nitric acid to combine with potash is in reality considerably greater than that of sulphuric acid*.

It has been found that the relative neutralizing powers of these, and of other acids, are almost independent of temperature, between 0° and

* A fuller account of this subject will be found in *Elementary Chemistry*, by Muir and Slater, or in J. Walker's *Introduction to Physical Chemistry*.

60°, and also of the nature of the base employed; so that potash may be replaced by soda, for example, without affecting the proportions of the acids neutralized. And thus it is possible to assign to each acid a number, called its *specific affinity constant*, which indicates its relative value in reactions.

The following table gives the approximate values of the specific affinity constants of a few acids:—

<i>Name.</i>	<i>Affinity constant.</i>
Hydrochloric acid	100
Nitric acid	99.6
Sulphuric acid	65.1
Oxalic acid	19.7
Acetic acid	0.4

The values given in this table have been deduced from the electric conductivities of the acids, for it is found that when the electric conductivities of acids are used to measure their affinities the values obtained agree with those based upon the study of chemical changes. According to modern views the conductivity of an electrolyte depends upon the proportion of free ions which it contains (331), and this agreement between the electric conductivity and the chemical activity of an electrolyte makes it seem probable that the latter also depends on the proportion of free ions. If this view be correct, a strong acid is an acid which is highly ionized; that is, which contains a large proportion of free ions.

321. Heat and chemical change. Every chemical change is accompanied by an evolution or by an absorption of energy*, which usually takes the form of an evolution or absorption of heat. It is difficult to measure the amount of heat evolved or absorbed in a given chemical change, such, for example, as the combination of two elements, partly because such changes usually are complicated by physical changes, which also involve the absorption or evolution of energy, partly because the necessary experiments are difficult to perform, and partly for other reasons. But there is every reason to believe that the thermal effect of any given chemical change is equal in quantity to the thermal effect of reversing that change. For example, that if Q units of heat are evolved when 12 grams of carbon unite with 32 grams of oxygen, then Q units of heat must be supplied to the 44 parts of carbon dioxide thus formed, in order to reproduce 12 parts of carbon and

* See p. 95.

32 parts of oxygen from them*. In short, there is every reason to believe that the principle of the Conservation of Energy, which states *That the total energy of any material system is a quantity which can neither be increased nor diminished by any action between the parts of the system, though it can be transformed into any of the forms of which energy is susceptible* (Clerk Maxwell), holds good in regard to all those transformations of energy which accompany chemical changes. The energy which disappears in the course of such a change as the transformation of water into oxygen and hydrogen is called *potential energy* to distinguish it from energy in such a form as heat, which may be attributed to the motion of the molecules concerned and therefore is known as *kinetic energy*.

An atom, or rather a pair of atoms which are capable of combining, may be compared to a stone of given weight held at a given distance away from the earth. The potential energy of the atoms becomes kinetic energy† if they combine, just as the potential energy of the stone becomes kinetic energy if the stone be allowed to fall to the earth. The elements may therefore be regarded as stores of energy, which becomes available for doing work when they combine. It is

interesting to remember that at present our chief available source of energy is the combination of carbon (coal) with the oxygen of the air.

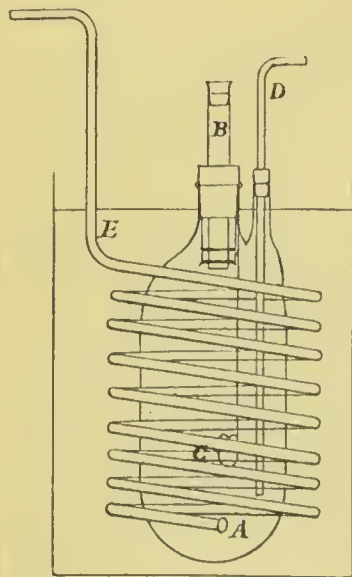


Fig. 111.

322. Measuring the heat evolved in chemical changes. As already stated, it is difficult to measure accurately the amounts of heat given out or absorbed in chemical changes. The methods employed vary according to circumstances, and it would be impossible here to describe them at all fully. It must be sufficient to give a single illustration.

Fig. 111 shows the apparatus employed by Berthelot to measure the thermal effect of the combustion of sulphur in oxygen.

It consists of a cylindrical vessel *A* made of thin hard glass, and of

* It will be noticed that it is here assumed that all the energy concerned in the change can be measured as heat.

† This usually, for the greater part, takes the form of heat.

about 400 c.c. capacity, surrounded by 1000 c.c. of water in a platinum calorimeter, which was prevented from losing or gaining heat from its environment during the experiment. The vessel *A* was provided with two necks, and oxygen was admitted through one of these by means of the tube *D*, while the wider neck carried a glass tube *B*, from which a small crucible *C*, containing sulphur, was suspended by a wire. Near the bottom of the vessel was an opening from which a spiral tube *E* carried off the gaseous products of the reaction thoroughly cooled by the water in the calorimeter.

In order that the exact amount of sulphur burnt might be known, the sulphur dioxide was collected during the experiment and its amount determined.

Then, the 'water equivalent' of the system being known, from independent experiments, and also its temperature at the beginning and end of the experiment, it was easy to ascertain the number of 'calories' evolved by the combustion of one or more grams of sulphur*.

Although it is not difficult to follow the comparatively simple operations involved in the above experiment, the making of such an experiment and the interpretation of the results obtained is less easy, and usually demands the performance of a number of other similar experiments. Thus 1 atomic proportion of native sulphur in grams yields when burnt 1 molecular proportion of sulphur dioxide, and its formation is accompanied by the evolution of 71,080 calories of heat, but we must not conclude that this number affords us a measure of the heat evolved by the combination of the atoms of sulphur and oxygen concerned in the change, for the 71,080 calories in question are really the sum of several quantities which are not necessarily all of a positive character:—

I. The sulphur used in the experiment is in the solid state. The product of its combustion is a gas, therefore the change investigated includes the volatilizing of some solid sulphur, and this physical change would be accompanied by the absorption of a definite amount of heat.

II. The sulphur and oxygen before they were burnt probably existed in molecules consisting of several atoms. These had to be broken up before sulphur dioxide (SO_2) could be formed, and these changes

* If suitably modified, the apparatus could be employed for studying the combustion of oil, wax, carbon, or even of hydrogen, and gaseous hydrocarbons.

also would be likely to be accompanied by the absorption of a definite quantity of heat in each case.

Therefore before we can ascertain the thermal effect of such a seemingly simple change as the combination of an atom of sulphur with two atoms of oxygen, we must find separately the thermal effects of the accompanying physical and chemical changes, as well as determine the heat of combustion of sulphur in the manner described above.

Exercises for the student.

1. What data would you require in order to ascertain the thermal effect of the union of—

- (a) An atom of chlorine with an atom of hydrogen ;
- (b) An atom of carbon with two atoms of oxygen ;
- (c) An atom of potassium with an atom of chlorine ?

Your solutions of these problems should be submitted to your teacher for criticism. If you are unable to state whether any given change is endothermic or exothermic, you may use the symbol $\pm$. Although chemical combinations between elements are sometimes endothermic, or absorb heat, what is known tends to show that combination between two atoms probably would be accompanied by an evolution of heat, and therefore that the separation of two or more atoms would be accompanied by an absorption of heat.

323. Heats of combustion of elements. The data given in the following tables are most of them derived from the researches of Julius Thomsen. Many other data, and a full account of the methods that have been employed by Thomsen and others, will be found in *The Elements of Thermal Chemistry*, by Pattison Muir and Wilson. They should be studied carefully, but should not be learnt by heart.

<i>Substance.</i>	<i>Product.</i>	<i>Heat produced by burning 1 atomic proportion in grams of each substance.</i>
1. Hydrogen . . .	H ₂ O	34,180 units.
2. Carbon . . .	CO	29,000
3. „ (CO + O) .	CO ₂	67,960
4. „ . . .	CO ₂	96,960
5. Wood Charcoal .	CO ₂	96,960 Amorphous.
6. Graphite . . .	CO ₂	93,560
7. Diamond . . .	CO ₂	93,350 } Crystalline.
Phosphorus		
8. Yellow . . .	P ₄ O ₁₀	184,950
9. Red . . .	P ₄ O ₁₀	163,430
10. Sulphur . . .	SO ₂	71,080

Problems.

1. Calculate how many units of heat would be evolved, or absorbed, if 1 gram of red phosphorus were changed into yellow phosphorus.
2. How many units of heat would be evolved, or absorbed, in transforming 3 grams of graphite into amorphous carbon?
3. How do you account for the fact that while the heat of formation of carbon monoxide is 29,000, that of the dioxide is considerably more than twice as great, viz. 96,960?

Heats of Combustion of some Carbon Compounds.

Marsh gas	209,000
Methyl alcohol	169,830
Ethyl alcohol	330,450
Ethylene	332,000
Benzene	787,950
Ethyl Ether	668,000

324. Heats of formation of molecular proportions of some important compounds:—

Hydrogen chloride	22,000	Nitric oxide	- 21,575
„ bromide	8,440	„ peroxide	- 2,005
„ iodide	- 6,040	Cyanogen	- 65,700
„ sulphide	4,740	Marsh gas	21,750
Sulphur dioxide	71,080	Acetylene	- 48,170
Ammonia	11,890	Carbon disulphide	- 26,010
Nitrous oxide	- 17,470		

325. Heats of neutralization of equivalent weights of some acids by soda:—

HF	16,270	HPO ₃	14,380
HCl	13,740	HCN	2,770
HBr	13,750	$\frac{1}{2}$ H ₂ SO ₄	15,690
HI	13,680	$\frac{1}{3}$ H ₃ PO ₄	11,343
H ₂ S	7,740	HC ₂ H ₃ O ₂	13,400
HNO ₃	13,680		

It is remarkable that so many acids evolve about the same amount of heat when an equivalent of an acid is neutralized by an equivalent of soda in dilute solutions. This has suggested the idea that the chief

change that really occurs in these cases consists in the formation of water; because, according to the theory of electrolytic dissociation (see 331), the acid and alkali taken and the salt produced are all more or less dissociated, whilst water, which is a non-conductor, dissociates to only a very small extent, or not at all.

The thermal phenomena which occur on neutralizing an acid of known molecular weight may be utilized in determining its basicity *, since a molecular proportion of a dibasic acid would generate about twice as much heat when neutralized as a similar proportion of a monobasic acid.

326. The stability of exothermic compounds. The study of the transformations of energy which accompany, or rather form part of, chemical changes, shows that, as a general rule in the case of allied compounds, those are most stable whose formation is accompanied by the greatest evolution of heat; whilst endothermic compounds, on the other hand, are usually instable in their character. Thus, the heats of formation of the halogen hydrides are as follows:—

<i>Compound.</i>	<i>Heat of formation.</i>
Hydrogen chloride	+ 22,000
„ bromide	+ 8,440
„ iodide	- 6,040

Now hydrogen chloride and hydrogen bromide are more readily formed from their elements than hydrogen iodide, and are more difficult to decompose by heat, and, further iodine is more easily displaced from hydrogen iodide by oxidizing agents than chlorine from hydrochloric acid or bromine from hydrogen bromide. But though it is tolerably safe to conclude that a compound whose formation is accompanied by a great evolution of heat will be stable, we must not be tempted to imagine that the above figures afford an exact measure of the respective attractions of chlorine, bromine, and iodine for hydrogen, for it is found that no such inference can be drawn safely.

327. Heat is often required to start a chemical action. Although many compounds decompose when heated, we have frequently found it necessary to raise the temperature of the substances used in our experiments in order to bring about chemical combination. Thus oxygen and hydrogen do not combine at ordinary temperatures; phosphorus is only inflammable when heated above its melting point;

* See 199.

iron will only burn in oxygen if it be first made hot, and many changes which occur at ordinary temperatures do not take place at very low ones*. From these facts it would appear that energy is sometimes required to bring the parts of a system into a state in which chemical action between them becomes possible.

Let us suppose that a stone lies in a depression near the top of a hill. This stone possesses a store of energy in virtue of its position, but though it is near the top of the hill it cannot fall, and hence its energy cannot become available to do work. If, however, a little energy from an outside source be spent upon it, if we move the stone to a position whence it is free to descend, it will at once roll down the hill, and its energy will become available, and may be utilized in various ways.

Now a piece of phosphorus placed in a vessel of oxygen at 0° may be compared to the stone in its first position. The two elements possess a considerable store of energy which would become available, mostly in the form of heat, if they combined. But before they can do this sufficient energy must be supplied to them to raise their temperature at some point to 45° . If this be done they will at once unite and evolve great quantities of heat.

The student will now understand that the statement that water consists of oxygen and hydrogen (and all similar statements) is only true in a limited sense, viz. that, by suitable treatment, it is possible to obtain from 18 parts of water 2 parts of hydrogen and 16 parts of oxygen, or, vice versa, that when 2 parts of hydrogen and 16 parts of oxygen disappear in a chemical change they are replaced by 18 parts of water. The customary mode of stating the relations of compounds and elements has a tendency to disguise the fact that the forming of water and other compounds involves something more than the mere coalescence of certain masses of matter:—

In a mixture of 16 parts of oxygen and 2 parts of hydrogen we have a definite mass of matter associated with a definite quantity of potential energy. In the water they form by combining, we have the same amount of matter, but in its new form this matter is associated with a smaller amount of potential energy than before. The water contains all the matter of the oxygen and hydrogen from which it was

* Prof. Dewar has shown that almost all chemical change ceases at the boiling-point of oxygen. There are a few exceptions; among these may be mentioned the darkening of a photographic plate.

formed, but part of the potential energy which was previously associated with that matter has become kinetic, and escaped as heat.

ELECTROLYSIS AND SOLUTIONS.

328. Electrolysis. (See also 39.) We have seen that when a current of electricity is passed through certain liquids, such as acidulated water, they are partly or wholly resolved into their elements. The following experiments will throw further light on this subject by teaching us —

1. Whether all substances conduct electricity.

2. Whether all those which conduct electricity are decomposed by the current, and if not, whether those which are decomposed belong to any particular class or classes of compounds.

EXPERIMENT 246. (*a*) Set up a small battery of galvanic cells (39). Connect the ends of the wires for an instant, and at the same time hold the needle of a small compass over and parallel to the wire. Notice how the magnet tends to set itself when the current flows; that is, whether it remains parallel to the wire, or takes a position at right angles to the flow of the current.

Disconnect the ends of the wires; notice, when you do so, whether the magnet returns to its former position, and whether the magnet again responds to the current if you once more allow electricity to flow through the wires.

A magnet then may be used to detect the passage of electric currents.

(*b*) Place a little quicksilver in a basin, dip the battery wires into the metal, bring the magnet near the wires as before and observe its movements. Do they show that a current of electricity passes through the wires and metal?

Notice, also, whether there are any signs that the metal is changed chemically by the passage of the current. Whether, for example, the metal is obviously affected as dilute sulphuric acid would be.

Conductors and electrolytes. Substances like the metals which conduct electricity without undergoing any permanent alteration, are called *conductors*, whilst substances which, like dilute sulphuric acid, are decomposed by the passage of electricity are called *electrolytes*.

EXPERIMENT 247. To find what classes of substances conduct electricity. 1. Dip your battery wires into distilled water in a U tube, then into water to which a little sulphuric acid has been added. Notice whether the current passes through water as it does

through acidulated water, and whether it gives off hydrogen and oxygen, the components of water, as in Experiment 36.

2. Try whether electricity will pass through solutions of a number of common solids, taking, for example, sugar, gum, solution of starch, and alcohol; try solutions of some salts, such as copper sulphate, sodium sulphate, and common salt, also mineral acids, such as hydrochloric acid; and also lead chloride fused in a crucible. Make lists of those which resist the passage of the current, and of those which transmit it; and draw up a table showing what you observe at each electrode in the case of those which are decomposed.

Your results should show that salts and mineral acids are electrolytes, but that organic substances conduct comparatively badly; also that hydrogen and the metals appear always at the kathode*, and a free acid together with oxygen, or else a non-metal†, at the anode.

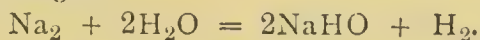
In these various results you have a number of illustrations of the general rule that solutions of organic compounds resist the passage of electricity, and that solutions containing salts or mineral acids in most cases conduct electrolytically.

329. Influence of the solvent on the results of electrolysis. If we compare the formulæ of the substances which proved to be electrolytes with those of the products of their electrolysis, we shall find that the former appear to be inconsistent with the latter.

Thus copper sulphate, to which for our present purpose we may give the formula CuSO_4 , appears to split into copper (Cu), oxygen (O_2), and an acid, and not into copper (Cu) and SO_4 , as we might have expected. Chemists explain this by supposing that the group SO_4 really makes its appearance at the positive electrode, but that it interacts with some of the water producing sulphuric acid and oxygen:—



Similarly, we did not get sodium and chlorine by electrolyzing salt, but chlorine at the positive electrode and free alkali (NaHO), with hydrogen (H_2), at the negative electrode, which may be accounted for by supposing that the sodium interacted with water, producing sodium hydroxide and hydrogen:—



* In the case of copper salts, the metal itself appears. In the case of salts of sodium and potassium, the metals when liberated act with the water, producing hydrogen and an alkali [verify this].

† In the above cases, chlorine is evolved from chlorides, oxygen and free acid from sulphates.

Problems for the student.—1. What compounds would you obtain by passing a current of electricity through a solution of potassium sulphate (K_2SO_4), and what gases would you expect to collect at the electrodes?

2. If a solution of silver sulphate be submitted to the action of a current of electricity, silver will be liberated at one electrode, oxygen and an acid at the other. How do you account for this?

EXPERIMENT 248. To study further the behaviour of salts under the influence of electric currents. Fuse some lead chloride in a small crucible, and dip the electrodes* of your battery into the fused salt. Notice that a current passes through the wire, that chlorine escapes at the positive electrode, and that drops of molten lead fall from the negative electrode. Now remove the lamp from under the crucible, and watch the behaviour of the magnet closely as the salt cools, to find whether the current is conducted by the solid salt.

The result obtained will tell you whether solid salts are electrolytes like those which are fused or in solution.

330. The quantitative laws of electrolysis, and electrochemical equivalents. Obtain, if you can, two electrolytic cells for decomposing water (Fig. 65); connect one of the electrodes of one cell with one of the electrodes of the other by a wire. Then connect the other two electrodes respectively with the anode and kathode of a battery in the usual manner†. Electrolysis will take place in both cells, and the respective volumes (and therefore the masses) of hydrogen and oxygen set free in one cell will be equal to those liberated during an equal time in the other cell. Again, if you place a solution of sulphate of copper in one of the decomposing cells, you will obtain at the anode of this cell as much oxygen as at the anode of that which contains acidulated water, and at the kathode of the former cell there will be formed a weight of copper which is *chemically equivalent* (see 86) to the hydrogen liberated in the latter‡. And similarly, if we set up a series of cells containing other electrolytes, the amounts of their respective components set free at the electrodes, when a given current of electricity is transmitted through them simultaneously, will be chemically equivalent.

* Small pencils of gas carbon, such as are used for arc lamps, make the best electrodes for this experiment.

† The two electrolytic cells should be provided with electrodes of equal areas.

‡ The student will not be able to verify this nor the succeeding statements at present.

These and similar facts are expressed by the *first* law of electrolysis, which may be stated as follows :—

1. *The amount of chemical effect produced by a current is equal at all points of an electrical circuit.*

It has also been found :—

2. *That the amount of a given element deposited at an electrode in a given time is proportional to the strength of the current.*

Thus *the amount of an element liberated at an electrode in one second is equal to the strength of the current multiplied by a number called the 'electro-chemical equivalent' of the element.*

The electro-chemical equivalents of the elements can be calculated from their chemical equivalents. Thus a quantity of electricity called a *coulomb* will liberate 0.000010384 gram of hydrogen from acidulated water. This may be termed the *electro-chemical equivalent* of hydrogen, and if we multiply it by the equivalent weight of copper (31.6), we get $0.000010384 \times 31.6 = 0.0003281$, the electro-chemical equivalent of copper*.

331. The hypothesis of electrolytic dissociation. We have learnt that the flow of a given quantity of electricity through an electrolyte is accompanied by the transference of a definite amount of matter to the electrodes (330). According to modern views concerning the nature of electrolysis, the electricity travels through the liquid with the matter transferred. It is supposed that every fluid electrolyte contains two sets of carriers of electricity, viz. a set which travels towards the negative electrode, when under the influence of an electromotive force, and a set which travels towards the positive electrode; these carriers of electricity are called *ions*, and they are supposed to be provided by the splitting up of the electrolyte. Thus, according to the electrolytic dissociation hypothesis, an aqueous solution of hydrochloric acid does not consist simply of molecules of water mixed with molecules of hydrochloric acid, but consists largely of molecules of water mixed with the ions of the latter substance. That is to say, the solution contains many† atoms of hydrogen, each carrying a definite charge of positive electricity, together with an equal number of atoms of chlorine carrying equal charges of negative electricity. We may suppose that as long as the electrolyte is not under the

* The student should study this subject more fully in a treatise on electricity, such as Prof. S. P. Thompson's *Electricity and Magnetism*.

† If the solution be very dilute, the acid will be, practically speaking, completely dissociated.

influence of an electromotive force, the *ions* move in every direction among the molecules of water, but that under the influence of such a force the positively charged hydrogen ions at once move towards the negative electrode, whilst the negatively charged chlorine ions travel towards the positive electrode. When the ions reach the electrodes they give up their charges, and thereupon the discharged atoms unite and make their appearance as hydrogen and chlorine respectively. The electrolysis of such a substance as common salt or dilute sulphuric acid follows a similar course, except that in the case of salt the positive ions consist of sodium, and that this when discharged produces soda and hydrogen with the water, and that in the case of sulphuric acid we have compound negative ions (SO_4), which also react with water when discharged, producing sulphuric acid and oxygen (329).

It will be seen that this hypothesis accounts in a satisfactory manner for the conducting power of electrolytes: for the appearance of the products of the decomposition of an electrolyte at places so remote from each other as the two electrodes; and for the constant relation that occurs between the quantity of electricity passing through a solution and amounts of the products of its decomposition (330).

As all acids, bases, and salts exhibit the property of electrolytic conduction to a greater or less extent, we must suppose that all these dissociate when they dissolve.

As hydrogen and the metals are attracted to the negative electrode we conclude that these carry positive charges and supply the positive ions, and that the non-metals, the salt radicles, and hydroxyl, on the other hand, carry negative charges, in the ionic state.

It must be added that all ions do not carry equal charges, though similar ions do so. Thus the charge carried by sulphion (SO_4), which combines with two atoms of hydrogen, is twice as great as that carried by an atom of chlorine, which only combines with one. And further, it must be explained that the fact that we are unable to detect the occurrence of dissociation in solutions of electrolytes indicates that the properties of charged atoms, if they exist, must differ from those of the corresponding molecules. Thus, we may suppose that the reason we do not recognize the presence of free chlorine in brine is this, that the charged atoms of chlorine want the colour, odour, and chemical properties by which we recognize chlorine in the free state.

If the student will now refer to the sections which deal with osmotic pressure (335), the freezing-points of solutions (92), and the heat of neutralization of acids (325), he will find that electrolytes exhibit certain

peculiarities in respect to all these phenomena, which become intelligible when they are studied by the light of the hypothesis of electrolytic dissociation.

332. Solutions. We have already learnt something about the solubility of solids in water (32 and 51), and considered some of the hypotheses by which chemists have sought to explain the phenomena of solution, so far as the dissolving of solids in water is concerned. But even if we exclude such cases as the dissolving of metals in acids from consideration for the present, there are other solvents besides water, and gases are soluble as well as solids.

Most gases dissolve in liquids to some extent, though often only to a very slight extent. As far as we know, quicksilver possesses less solvent power for gases than any other liquid.

The volume of a given gas which can be dissolved by a given volume of a liquid depends on the nature of the gas and of the liquid, and on the temperature and pressure at which the gas is held in solution. Gases are less soluble in hot water than in cold, and hence a liquid saturated at a low temperature will give off part of its gas if its temperature be raised.

The solubility of a gas is usually expressed by stating the *volume* (not the mass) which will dissolve in one volume of the solvent at 0° , this volume being known as the 'coefficient of solubility or absorption' of the gas for the given solvent.

Table of approximate coefficients of solubility of the known gases as determined by Bunsen and others.*

Hydrogen	0.02
Nitrogen	0.02
Oxygen	0.04 †
Atmospheric air	0.024
Nitrous oxide	1.30
Carbonic oxide	0.03
Carbon dioxide	1.80
Marsh gas	0.05
Ethylene	0.25
Hydrogen sulphide	4.37
„ chloride	505.0
Sulphur dioxide	79.79
Chlorine	2.58 (at 10°)
Ammonia	1148.8

* The experimental details may be sought in *Solutions* (Ostwald).

† A later determination gives 0.049.

333. Henry and Dalton's Law. The *mass* of a given gas dissolved by a given volume of a given solvent is proportional to the pressure exerted by the gas, or in other words the *volume* of gas dissolved by a given volume of a given solvent is always the same, provided that the gas and the solvent exert no chemical attraction upon one another.

Thus, 1000 c.c. of water dissolve 0.0576 gram of oxygen at 760 mm. and 0° , but will only dissolve 0.0288 gram at 380 mm. and 0° . But the volume of the gas will be 40 c.c. in each case, for 0.0586 gram of oxygen at 760 mm. occupies the same volume as half that mass at 380 mm. (see Boyle's Law).

The fact that we can increase the mass of a gas dissolved by a given mass of water, by increasing its pressure, is well illustrated by the aerated waters in which carbon dioxide has been dissolved under pressure.

334. The solubility of solids and liquids. We have already learnt some of the more important facts in connexion with

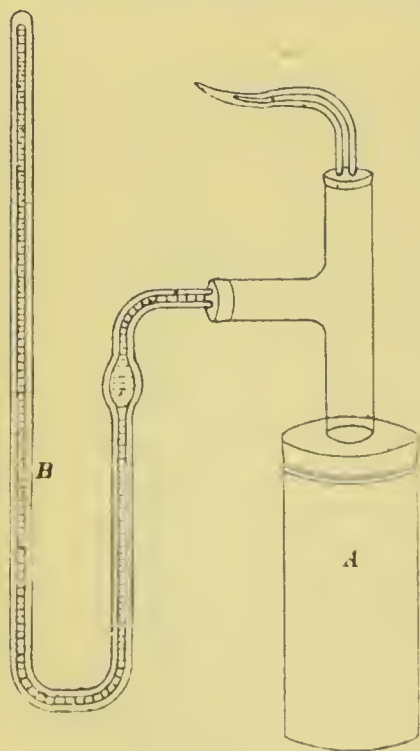


Fig. 112.

this subject. For example, that as a rule, salts are more soluble in hot water than in cold, and that not a few are practically speaking insoluble; that other liquids, such as alcohol and carbon disulphide, may often be substituted for water with advantage. Again, we have learnt that the freezing-points of the solutions of a large class of substances are below those of the solvents, and exhibit definite relations to the molecular weights of the substances in solution. And we have also learnt something about the chief facts of liquid diffusion. We may proceed to consider some remarkable phenomena which were for long overlooked.

335. Osmotic pressure. If a clay vessel *A* be provided with a suitable membrane, by depositing copper ferrocyanide* within its pores,

* For details see *Solutions*, by Ostwald, chap. v.

filled with a dilute solution of sugar, nitre, or some other solid, connected with a manometer *B*, and plunged in a vessel of water, the internal pressure will rise to a very remarkable extent. The annexed table gives the pressures obtained with 1 per cent. solutions of the substances mentioned. They are measured in centimetres of mercury:—

<i>Substance.</i>	<i>Pressure produced.</i>
Cane sugar	47.1 cm.
Nitre	178 „
Potassium sulphate	193 „

The separating film cannot be the cause of these remarkable phenomena, although the nature of the film affects the results obtained, for if the vessel be filled with water and plunged in a vessel of water no increase of internal pressure occurs. Moreover, it is found that the pressures produced in the case of solutions of any given solid are proportional to the concentration of the solutions employed, and thus it seems to be established that the 'osmotic pressures of solutions depend on the nature of the substances dissolved, and that they might be employed for determining the strengths of solutions.'

Influence of Pressure and Temperature. As stated above, the osmotic pressures of solutions of a given solid are proportional to their concentrations—thus, whilst a 1 per cent. solution of sugar gives a pressure of 53.8 cm., a 4 per cent. solution gives 208.2 cm., and a 6 per cent. solution 307.5 cm.—so that the osmotic pressure of a given solution is related to its concentration, as the pressure of a gas is related to its density.

It has been shown further that osmotic pressure increases regularly with rise of temperature much as the pressure of a gas kept at constant volume increases when it is warmed.

With a 1 per cent. solution of sugar the following results were obtained by Pfeffer, who first investigated this subject by the method described above:—

<i>Temperature.</i>	<i>Pressure.</i>
6.8°	50.5 cm.
13.8°	52.2 „
14.2°	53.1 „
22.0°	54.8 „

Lastly, it has been found that quantities of dissolved substances, which are in the ratio of the molecular weights of those substances,

exert equal osmotic pressures at equal temperatures. That is to say, the osmotic pressure of n molecules of a substance A is equal to the osmotic pressure of n molecules of another substance B , so that the osmotic pressures of A and B might be used for measuring their relative molecular weights*.

If the student compares what he has just learnt about osmotic pressure with the three gaseous laws, he will perceive a remarkable analogy between these laws and those which govern osmotic pressure.

The first law, that osmotic pressure increases in proportion to the concentration of the dissolved substances, corresponds to Boyle's law.

The second law, that the osmotic pressure of a given solution is proportional to its absolute temperature, corresponds to Charles's law.

The third law, which connects osmotic pressure with the molecular weights of substances in solution, corresponds to Avogadro's hypothesis.

In order to explain these remarkable analogies between substances in dilute solutions and in the gaseous state, van 't Hoff has suggested that if we regard solutions as mere homogeneous mixtures of their components, in which the molecules of the solvents and of the substances dissolved may be supposed, for most purposes, to be without influence upon one another, then we may consider that the molecules of dissolved solids are in a similar condition to those of gases. For like the molecules of gases they will be far apart, outside the range of their mutual attractions, and, though in constant motion, they will only come into contact occasionally. Thus only those of their properties will come into play which are influenced by the number of molecules in unit volume of the liquid. If this suggestion be accepted we may carry over to dilute solutions all that we know to hold good for the properties of gases, so far as they relate to pressure, volume, and temperature, provided that we substitute the osmotic pressure of liquids for the pressure of gases.

It was pointed out above that the molecular weights of soluble substances might be deduced from their osmotic pressures. Experimental difficulties have prevented this method from coming into use up to the present, but other properties of solutions, such as the depression of the freezing-points and the elevation of the boiling-

* This is not true of electrolytes.

points of solvents by the addition of known masses of soluble substances, are frequently employed.

The molecular weights deduced from the freezing-points and boiling-points of dilute solutions are, with certain important exceptions, generally concordant with those calculated from other data in those cases in which they can be compared, but this is not true in the case of electrolytes. The results obtained with acids, bases, and salts suggest that there are more molecules in given volumes of their solutions than we should find if we based our calculations upon other data *. It will be seen that this suggests that electrolytes undergo dissociation when they dissolve, a conclusion which harmonizes with the hypothesis of electrolytic dissociation discussed in 331. The student must, however, consult one of the larger treatises for further details on this part of the subject †.

CHAPTER XXI

SPECTRUM ANALYSIS

336. The Spectroscope. In various parts of this book reference is made to the spectra of the elements, and therefore a short account of the spectroscope and its uses is added for the assistance of those who have not yet studied Light.

If a pencil of sunlight be allowed to pass through a fine hole, and then to fall upon a sheet of white paper in a dark room, it will form a round luminous image of the sun on the paper screen.

If the light is made to pass through a triangular glass prism on its road to the screen, the pencil of light emerging from the prism will be found to be bent towards the base of the prism, and it will produce on the screen a band, more or less rounded at the ends, which exhibits in succession all the colours of the rainbow. This is the spectrum of the sun.

Newton, who first made the above experiment, concluded from it

* For the physical methods of finding molecular weights, see 91 and 92.

† The student would do well to read the passages on the subject of 'Solutions' in *Chemical Theory for Beginners*, by Drs. Dobbin and Walker. Fuller accounts of the subject will be found in Mr. M. M. P. Muir's translation of Ostwald's work on *Solutions* and in Dr. J. Walker's *Introduction to Physical Chemistry*.

that white light is not homogeneous, but made up of the seven colours of the spectrum—violet, indigo, blue, green, yellow, orange, red, and he showed that when they were recombined they again produced white light.

A student can hardly carry out the above experiment in a chemical laboratory. But he can make a somewhat similar experiment by means of the spectroscope, an instrument invented by Kirchhoff and Bunsen for studying spectra.

A simple and inexpensive form of spectroscope * is shown in Fig. 113. It consists of a brass tube, which has, at one end *R*, a cap carrying a fine slit, behind an opening *O*, which admits light to the interior of the tube. It is desirable that means should be provided for adjusting the width of this slit. Inside the tube at *a a* is a small lens whose focus coincides with the slit; hence if *O* be held to a source of light parallel rays of light fall upon the train of prisms *C C C F F*. These lenses decompose the light, producing a spectrum † which can be seen by the eye at *E*.

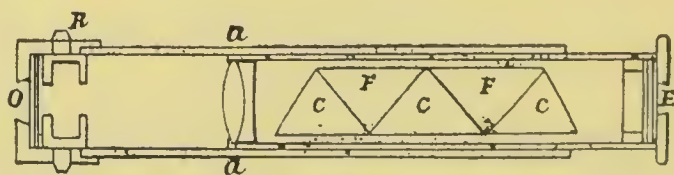


Fig. 113.

A more powerful and exact form of spectroscope consists of a prism, or train of prisms, *W* mounted on a table *D* (Fig. 114), which also carries a tube, containing a lens; this tube has an adjustable slit at *B*. The light from the slit falls on the prisms and the spectrum produced is observed by means of a telescope *C*. The telescope is carried by an arm which works over a scale of degrees marked on the edge of the table. Inside the telescope is a pair of cross wires, by means of which it is possible to identify any particular part of a spectrum.

EXPERIMENT 249. 1. Hold the slit of your spectroscope towards a white cloud and place your eye at *E*. You will see a band of light resembling a strip of a rainbow, and showing all the colours enumerated above (see frontispiece).

2. Direct the slit of the spectroscope towards a gas or candle flame.

* Such instruments can be purchased at from £1 1s. upwards. An excellent form of direct-vision spectroscope, costing £3 3s., has lately been introduced by Mr. Hilger.

† The explanation of this must be sought in a treatise on light.

You will observe a similar spectrum, for the source of light in this case, as in the case of sunlight, is highly ignited solid matter.

3. Hold small fragments of common salt, lithium chloride, and thallium chloride in a Bunsen flame by means of a platinum wire, and examine the flame with the spectroscope. You will see a few bright lines separated by dark intervals in place of the continuous band of colour. The sodium will give a single yellow line; lithium a red line, and also an orange line; and thallium, a striking green line. These bright lines are produced by ignited gases or vapours, and you will find that a given element, e.g. sodium, always gives exactly the same line or lines, so that each gas and vapour may be identified by its spectrum.

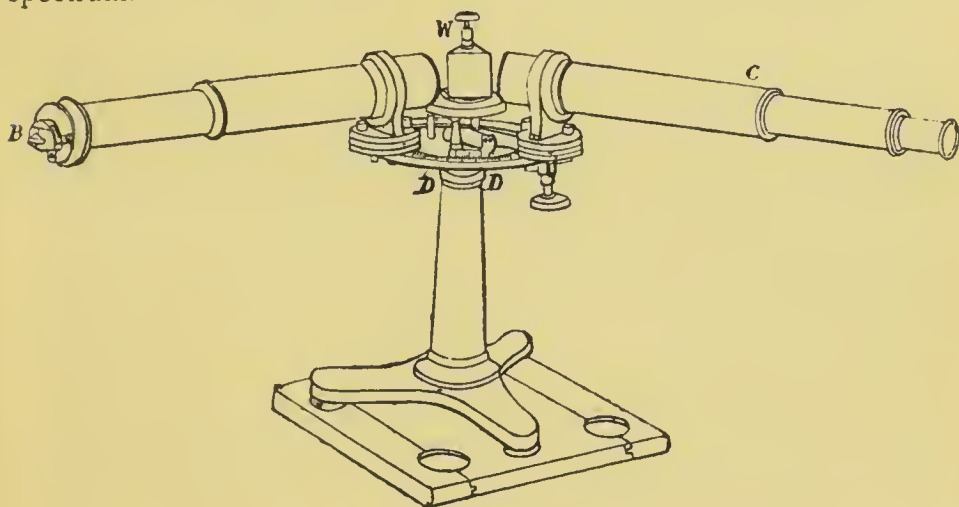


Fig. 114.

The spectroscope has not only been useful to analysts, it has also been of immense value to chemists, physicists, and astronomers. Many new elements have been recognized by its aid: thus a few years ago, Dr. Ramsay when examining a gas obtained by treating the mineral cleveite with sulphuric acid noticed that a line in its spectrum corresponded with a line in the solar spectrum ascribed to helium, an element which previously had only been detected in the sun. And it was largely by the help of the spectroscope that Lord Rayleigh and Prof. Ramsay were able to identify argon in the air.

The method of spectroscopic analysis is so delicate that 0.0000005 of a milligram of sodium gives a distinct spectrum, and exceedingly small quantities of other elements may also be detected with certainty by a skilled observer.

EXPERIMENT 250. The spectra of liquids. Absorption spectra. Obtain a little coloured liquid, such as some very dilute red ink. Hold a small tube of this liquid before the slit of the spectroscope, and place a bright source of light behind it. On looking through the spectroscope you will see an intermittent band of light, a continuous spectrum with certain parts missing. This is an 'absorption spectrum.' Coloured liquids of definite composition and coloured gases may be recognized by such spectra; they are caused by the liquid or vapour absorbing some of the radiations which collectively make up white light, and transmitting others which alone are seen.

In legal cases, blood and blood-stains are recognized by their characteristic spectra.

Fraunhofer's lines. If you examine solar light with a good spectroscope you will find that the solar spectrum is not really continuous, but that a number of very narrow dark lines occur in it * (see frontispiece). These dark lines were first carefully studied by Fraunhofer, and it has been shown, by methods which cannot here be discussed, that they correspond in many cases to the bright lines given by the ignited vapours of well known elements.

Thus, for example, a number of these dark lines coincide with lines present in the spectrum of iron, and the lines of various other metals are also thus represented in the solar spectrum.

The Fraunhofer lines can easily be imitated in the laboratory by allowing white light to pass through the vapour of sodium, and then to fall upon the slit of the spectroscope. When this is done a dark band, corresponding to the sodium line (frontispiece, Fig. 2), is seen in the spectrum. This experiment affords a clue to the origin of the Fraunhofer lines. They are caused by the passage of white light from the body of the sun through the vapours which make up its atmosphere, and therefore they afford us a means of learning what that atmosphere is composed of.

Up to the present between thirty and forty elements have been identified in the solar atmosphere, including hydrogen, iron, sodium, calcium, magnesium, and many other metals.

* M. Hilger's direct-vision spectroscope shows these lines well.

CHAPTER XXII

CRYSTALLOGRAPHY

337. The student has already learnt that certain substances do or do not occur in crystals, but probably he has a very vague idea of the exact meaning of the word crystal.

A crystal may be defined as a solid homogeneous body bounded by plane faces, arranged in a regular manner which is constant for each particular substance. This does not mean that every crystal of sulphur exactly resembles every other crystal of that substance, for the conditions under which crystals grow modify their forms. A crystal of sulphur grown on the bottom of a pan, for example, would not exactly resemble one grown when suspended freely in the solution above it. But although the number of faces which bound the crystals of a given solid, and also the shapes of those faces, may vary with variations in the conditions at the time of their formation, the geometrical relation which the faces bear to one another, and the manner in which they occur in groups, are characteristic for each substance.

The complete examination of the form of a crystalline substance demands much knowledge and considerable experimental skill, and would be quite beyond the powers of a beginner. But the following remarks will help the reader to understand that the subject is both interesting and important, and should enable him to recognize such of the terms relating to crystals as are likely to occur in elementary chemical textbooks.

Crystals are usually formed either by separation from solution, as in the case of many salts (Expt. 29), or by the solidifying of a fused mass, as in the case of sulphur (Expt. 30), or by sublimation, as in the case of arsenic (Expt. 32).

It is often possible to decide whether a solid is of crystalline or amorphous structure by the character of its fracture, if its particles are sufficiently large to be examined with the naked eye or by a lens. Amorphous substances usually show a conchoidal fracture, like that of glass, when they are broken, whilst the fragments of a crystalline solid often exhibit, more or less clearly, plane faces of greater or smaller area.

The tendency of crystals to split in definite directions is known as *cleavage*, and is to be regarded as evidence that they possess a definite structure.

338. Dimorphism. We have already learnt that a given substance may exhibit more than one crystalline form. Thus it will be remembered that carbon exists in two crystalline forms as graphite and diamond. And again, that sulphur was obtained in octahedra by evaporating a solution of the element in carbon disulphide, but took the form of needle-like prisms when deposited from molten sulphur. Such substances are said to be *dimorphous*. It will be remembered also that in both cases the difference of crystalline form is accompanied by difference of colour; and these crystals differ similarly in regard to their other properties. Thus octahedral sulphur melts at 114.5° , and its density is 2.05, whilst the melting-point of prismatic sulphur is 120° , and its density 1.96. Hence one of these varieties of sulphur can be distinguished from the other, even in the state of a fine powder.

Isomorphism. It was shown many years ago by Mitscherlich that certain compounds which form crystals of the same or nearly the same form can be deposited mingled in the same crystals, without alteration of crystalline form, from liquids containing both. Such substances are said to be *isomorphous*, and it has been observed that the molecules of isomorphous substances are similarly constituted. Various cases of isomorphism have already been mentioned: see alums (201), arsenates (270), and phosphates (259).

339. Classification of crystals. If we suppose the molecules of crystals to be arranged about certain sets of imaginary lines called *axes*, we can classify their various forms in six groups or *systems*, each of which will include prismatic and pyramidal forms. In the following diagrams the axes are indicated by the dotted lines. It is a good practice to cut models of the various crystals in soap. Their axes can then be indicated by inserting wires in suitable directions.

I. *The cubic, regular, or monometric system* (Figs. 115, 115A). Crystals belonging to this class have three equal axes (aaa), all at right angles. Many substances with which you are acquainted belong to this system; for example, the diamond, many of the metals, common salt, potassium iodide, alum, and iron pyrites.

Crystals belonging to the cubic system are simpler in respect to their physical properties than the rest. Thus they conduct heat and

electricity equally in all directions, which other crystals do not, and they lack the power of double refraction which is possessed by crystals belonging to other systems.

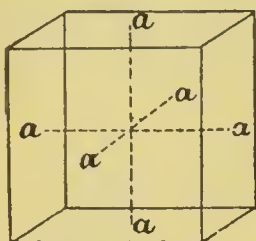


Fig. 115.

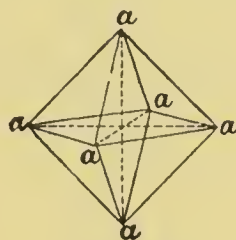


Fig. 115 A.

II. *The dimetric or quadratic system* (Figs. 116, 117). The crystals of this system have also three axes which are at right angles to each

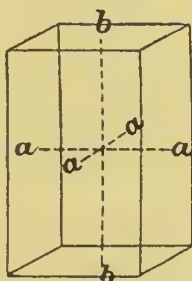


Fig. 116.

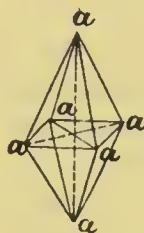


Fig. 117.

other, but only two ($a\ a$) are of equal length, the third (b , Fig. 116) being longer or shorter than the other two.

Crystals of ferrocyanide of potassium belong to this system.

III. *The trimetric or right prismatic system* (Figs. 118, 119). Crystals

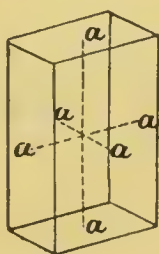


Fig. 118.

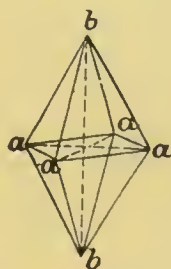


Fig. 119.

belonging to this system have three axes, all of unequal length, and placed at right angles. Thus trimetric prisms rest on rectangular

bases, but not on square bases like those of class II. Nitre and octahedral sulphur belong to this system.

IV. *The monoclinic system* (Figs. 120, 121). In this there are three axes, which are unequal. Two ($a\ a$) are at right angles, but the third ($b\ b$) is inclined to the plane of the other two. Prismatic sulphur and green vitriol are familiar examples.

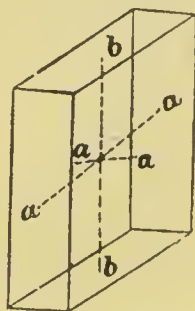


Fig. 120.

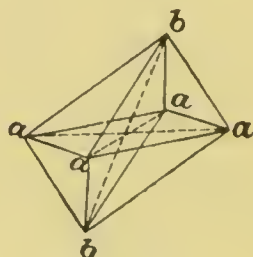


Fig. 121.

V. *The triclinic or doubly oblique system*. The crystals of this class have three axes, which may be all unequal in length, and are all inclined to one another. Copper sulphate affords an example of triclinic crystals.

VI. *The hexagonal system* (Figs. 122, 123, 124). Crystals of this class have four axes, three ($a\ a\ a$) of equal length, all in the same plane, and inclined to one another at angles of 60° . The fourth axis ($b\ b$) is vertical to the plane of the other three.

Quartz, calc-spar, and ice are examples of hexagonal crystals. The first often crystallizes in well-defined hexagonal prisms with pyramidal ends. One or two of the examples quoted should be examined by the student in this and every other case.

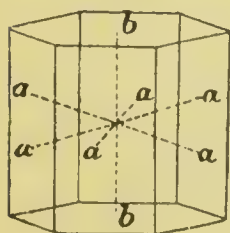


Fig. 122.

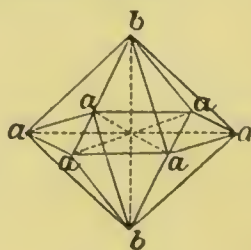


Fig. 123.

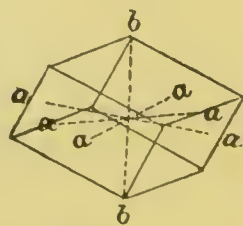


Fig. 124.

As has already been explained, under ordinary circumstances the different faces of a crystal are frequently unequally exposed to the liquid or vapour in which they form, whereby new figures may be generated. Thus, if a cubical crystal be prevented from growing

at its solid angles, it will form an octahedron, as may easily be seen by cutting a cube of soap, or potato, and then gradually slicing away its eight corners till new faces meet as shown below (Figs. 125-127).

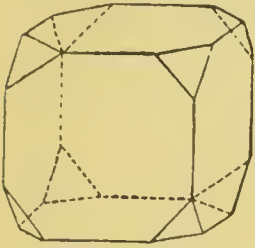


Fig. 125.

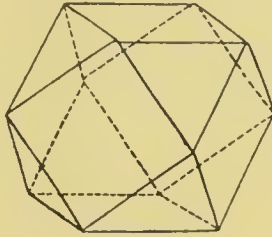


Fig. 126.

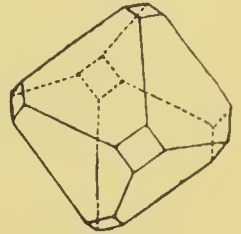


Fig. 127.

When solid angles are thus replaced by planes they are said to be *truncated*.

Hemihedral crystals. If the student will cut out a model of an octahedral crystal (Fig. 115 A) from a piece of potato, and then cut four tetrahedra of such size that their faces will match the faces of the octahedron, and apply the four tetrahedra to the alternate faces of the octahedron, he will obtain a tetrahedron which may be supposed to have been formed by the growth of the alternate faces of the octahedron. The growth of the alternate planes of a crystal to the exclusion of the rest generates what are known as hemihedral forms.

Crystals can also be modified by two crystals combining to give a more complex form.

PART V

THE METALS

CHAPTER XXIII

INTRODUCTORY STUDIES CONCERNING THE METALS

340. Producing metals on the small scale by heat and electrolysis. The methods employed for reducing compounds of the metals are numerous. In a few cases their oxides can be reduced by heat, but usually a reducing agent must be employed. Often the fused chloride of the metal, or a solution of one of its salts, may be electrolyzed. On the large scale various special processes are made use of, and some of these will be briefly mentioned at later stages. The following experiments will afford the beginner a suitable introduction to the more technical studies which follow.

EXPERIMENT 251. To prepare mercury by heating its oxide. Place about 2 grams of oxide of mercury in a piece of hard-glass tube *A* (Fig. 128), 15 or 20 cm. long, sealed at one end, and drawn out at *B*.

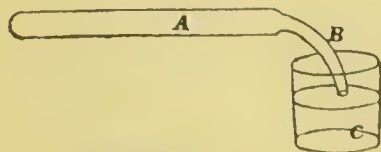


Fig. 128.

Place the tube over a gas burner with its end *A* slightly raised, and let the tip of *B* touch the surface of the water in *C*. Heat *A* and its contents pretty strongly. Oxygen will escape, and quicksilver will condense on the cooler parts of the tube. If the quicksilver be driven from the tube by heat, it will collect under the water in *C*. The drops of mercury may be made to run together by warming them under a little strong hydrochloric acid. Wash the product with a little

water, decant the water and dry the quicksilver by means of bibulous paper.

EXPERIMENT 252. To prepare metallic silver from its oxide or nitrate. Place 1 or 2 grams of oxide or nitrate of silver in a porcelain crucible; heat the crucible, gently at first, then more strongly by means of a blow-pipe flame or in a furnace*, and allow it to cool. On examining its contents, you will find it contains a more or less coherent mass of silver. If this be reheated to very bright redness in a muffle furnace it will yield a small button of the metal.

EXPERIMENT 253. To prepare platinum by decomposing its chloride by heat. Heat a decigram of chloride of platinum (PtCl_4) or, better, of the double chloride of platinum and ammonium ($2\text{NH}_4\text{Cl}, \text{PtCl}_4$), in a crucible. A dark but more or less metallic powder will remain. You may heat this powder to the highest temperature obtainable by means of a furnace without melting it; but it can be melted by means of the oxyhydrogen flame in a cavity in a piece of good quicklime.

Mercury, silver, platinum, and gold can be prepared by heating their oxides, carbonates, and nitrates, and platinum and gold by heating their chlorides; such salts as the oxalates can be reduced by heat in the case of these and several other metals.

EXPERIMENT 254. To prepare an easily fusible metal, such as lead, from its chloride by electrolysis. Melt about an ounce of lead chloride in a small crucible. Attach two small rods of gas carbon to the wires from your battery (39), and dip them into the molten salt, taking care that they do not come into contact. Bubbles of chlorine will at once be given off, and metallic lead will fall to the bottom of the crucible. After ten or fifteen minutes allow the crucible to cool, and separate the lead from the remaining salt.

Aluminium has been prepared by an electrolytic method from the double chloride ($2\text{NaCl}, \text{Al}_2\text{Cl}_6$), and lithium may be obtained by a somewhat similar process from its fused chloride, but as metallic lithium is lighter than the melted chloride, and combustible in air, it is apt to rise to the surface of the salt and burn. Consequently special precautions must be taken in order to secure it.

EXPERIMENT 255. To obtain copper by electrolyzing a solution of one of its salts. Pass the current from your battery through

* The decomposition of the nitrate is facilitated by passing a stream of coal gas through the crucible whilst you heat the salt.

a solution containing 5 to 10 per cent. of copper sulphate, using a sheet of copper for the kathode and a sheet of platinum for the anode (Fig. 129). Metallic copper will be deposited on the kathode, oxygen will be given off at the anode. Ultimately the solution will contain only dilute sulphuric acid. This result may be represented as follows (see also 329):—

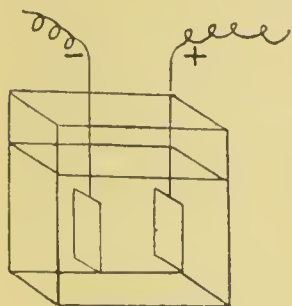
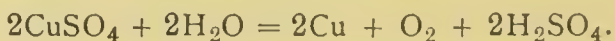


Fig. 129.



The deposit of copper may fall to pieces when detached from the electrode, and it will probably acquire a dark colour, owing to superficial oxidation, when it is removed from the liquid to dry it. It may be fused to an ingot under potassium cyanide, in a muffle furnace.

The electrolytic method of depositing copper is much used for making copies of woodcuts for illustrating books, and for similar purposes.

Electroplating. In the process of electroplating, by which the less expensive metals are coated with silver, or gold, the objects to be plated are attached to the kathode of a galvanic battery, and immersed in a suitable bath containing the double cyanide of silver (or gold) and potassium. A plate of silver is used as the anode of the system. Under the influence of the current, silver is deposited on the objects which form the kathode, whilst the cyanogen liberated at the anode simultaneously dissolves an equivalent quantity of silver, and thus the strength of the silvering solution remains unaltered.

EXPERIMENT 256. To plate copper. Add an aqueous solution containing 5 per cent. of silver nitrate to a 4 per cent. solution of cyanide of potassium till a permanent precipitate begins to form, and decant the clear solution thus made. Clean a small piece of sheet copper and also a piece of sheet silver very carefully with a scratch brush, or emery paper, and weigh them. Connect the silver with the anode and the copper with the kathode of a galvanic cell, dip them in the silvering solution *, and protect the solution from the air by pouring a thin layer of mineral oil upon it. The copper will soon acquire a coat of silver. Let the current flow for two or three hours, then dry

* Other substances are often added to the silvering solution. Thus, if bright deposit of silver is needed, carbon disulphide is used in the bath.

and reweigh the pieces of metal. Ascertain whether the silver has lost weight, and whether the copper has gained correspondingly.

341. Obtaining metals with the aid of reducing agents.

Metals are sometimes obtained by reducing their oxides with hydrogen, as we reduced iron rust in Experiment 53, but on the large scale carbon monoxide is chiefly employed for this purpose.

EXPERIMENT 257. To reduce iron oxide by means of carbon monoxide. Pack a piece of hard-glass tube, *C* (Fig. 130), about 35 cm. in length, with small fragments of well-made charcoal to *C*, and place iron rust

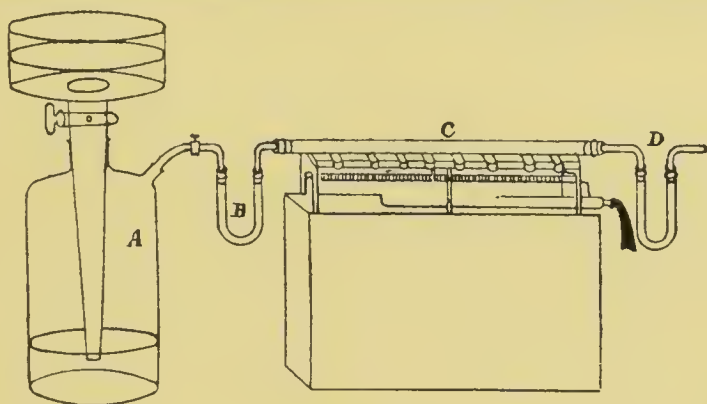
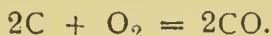
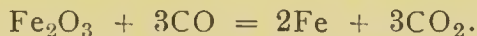


Fig. 130.

between *C* and *D*. Then, having heated the tube to redness, pass a *slow* current of oxygen over the red-hot material. Notice that the carbon is gradually consumed. Most of it is converted into the monoxide (CO):—



Notice also that the iron rust is reduced to metallic iron:—

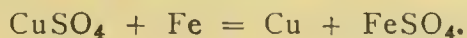


The iron and the gas which escapes should be tested.

Similar experiments may be made with other metallic oxides, such as those of copper or nickel.

EXPERIMENT 258. To reduce soluble compounds of metals by means of other metals higher in the electro-chemical series.

1. Place a strip of sheet iron in a strong solution of a copper salt. Copper will at once be deposited on the iron. When the blue colour of the copper salt has disappeared, test the solution for iron and copper (see pp. 461 and 479). You will find that the iron has replaced the copper. The change may be expressed as follows:—



This method of extracting copper from solutions is extensively practised on the large scale.

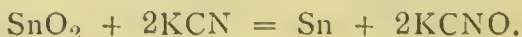
2. Introduce a weighed piece of zinc-foil into some solution of stannous chloride. Notice that the zinc becomes covered with a crystalline fur-like crust. This consists of minute crystals of metallic tin.

When a considerable deposit has formed, strip it from the zinc and wash, drain, and dry it. If it be heated moderately under a little cyanide of potassium, in a crucible, it will run into a single globule. On reweighing the zinc, you will find that much of it has disappeared:—



3. If you possess a good magnifying lens, or, better, a microscope, place a drop or two of solution of silver nitrate on a sheet of glass, add a minute scrap of zinc or magnesium, and watch it with your magnifier. Crystals of silver will shoot from the zinc in every direction. They present a most beautiful appearance, especially if they are brightly illuminated. This method of reducing compounds of the metals has been extensively used. Thus magnesium and beryllium have been made by reducing their chlorides, at a high temperature, with metallic sodium. Copper, as mentioned above, is extensively prepared by the action of scrap iron on solutions of its sulphate. And aluminium was at one time made by plunging large masses of metallic sodium into vessels filled with molten cryolite ($\text{AlF}_3, 3\text{NaF}$).

EXPERIMENT 259. The use of cyanide of potassium for reducing metallic oxides. (This experiment should be omitted by young students.) Melt some cyanide of potassium in a porcelain crucible, or in an iron basin, over a Bunsen burner, taking care to avoid handling the cyanide. Then add, little by little, some oxide of tin or oxide of lead, pour the contents of the crucible on an iron plate, and separate the metal from the accompanying salt when it is cool. Cyanide of potassium is chiefly used for reducing metals in small quantities in chemical analysis, but it is also occasionally employed on a rather larger scale in the laboratory. Its action depends on the readiness with which it takes up oxygen to form a cyanate (KCNO). Thus, with oxide of tin (SnO_2) the following change occurs:—



EXPERIMENT 260. To reduce oxide of lead by means of carbon at a high temperature. Carbon is largely used as a reducing

agent by metallurgists. Both oxide of tin and oxide of zinc are reduced by heating them strongly with small coal or charcoal, and oxide of lead may be reduced quite easily.

Heat strongly some red lead, or litharge, well mixed with an equal weight of finely divided carbon, in the form of lampblack, and with a rather larger proportion of sodium carbonate, in a well covered crucible. Allow the crucible to cool, and examine its contents. A mass of metallic lead will be found at its bottom.

342. Metallic oxides. We have already learnt that many metallic oxides interact with acids giving salts and water, and that such oxides are said to be *basic* (112).

The following are some of the chief general modes of obtaining those basic oxides which do not occur free in nature :—

1. By heating their carbonates, or nitrates, and in some cases other salts.
2. By precipitating solutions of metallic salts by means of alkalis, such as potash or soda, and igniting the precipitated hydroxides.
3. By direct oxidation of metals in air at suitable temperatures.
4. By the action of metals on water.

343. Preparing metallic oxides by heating their carbonates or nitrates. EXPERIMENT 261. To prepare 10 grams of quicklime (CaO) from limestone (CaCO₃).

Heat a suitable quantity of marble in small fragments in a platinum or nickel crucible * as strongly as possible in the flame of a blow-pipe, or in a muffle furnace, for 10 or 15 minutes, and allow it to cool. Throw a little water on the residue. If it be good lime, it will fall to a powder when this is done. Dissolve this powder in dilute hydrochloric acid. It will not effervesce with the acid, for the limestone has been converted into quicklime (CaO) :—



Nearly all carbonates, except those of the metals of the alkalis, yield oxides when strongly heated.

EXPERIMENT 262. To prepare about 10 grams of oxide of copper (CuO) by igniting copper nitrate (Cu(NO₃)₂·3H₂O). Heat a suitable weight of nitrate of copper strongly in a crucible in a fume closet, or in the open air. Notice that red fumes of nitric

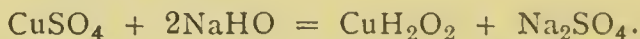
* The oxygen furnace of Messrs. Fletcher, Russell & Co., of Warrington, may be used, but in that case a salamander crucible should be employed.

peroxide (N_2O_4) (237) are evolved freely, and that a black solid remains. The black residue is oxide of copper (CuO).

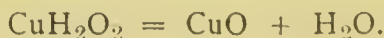
EXPERIMENT 263. To prepare six grams of iron oxide (Fe_2O_3) by heating ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Heat the required weight of iron sulphate, gently, in a porcelain crucible, until most of its water of crystallization is expelled, then heat the residue more strongly. A brown residue of ferric oxide (Fe_2O_3) will remain in the crucible.

Some other salts of oxyacids behave similarly, but those which contain much carbon may leave a metallic residue, mixed with some carbon. The salts of phosphoric, silicic, and boric acid are not converted into oxides even at very high temperatures, and the sulphates of calcium, barium, and strontium also bear a high temperature without decomposing.

344. Preparing metallic oxides by precipitation. **EXPERIMENT 264.** To prepare 8 grams of copper oxide. Dissolve the proper amount of cupric sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in some cold water, and add solution of caustic soda (NaHO) until the solution becomes alkaline to litmus. A light-coloured precipitate of cupric hydroxide (CuH_2O_2) will fall:—

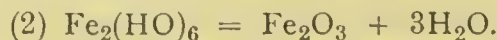
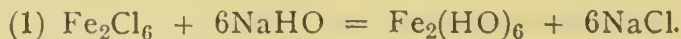


Then heat the flask and its contents on a sand bath. The hydroxide will gradually become black owing to the production of black oxide of copper:—



Heat the contents of the vessel to the boiling point for a few minutes, then collect, wash, and dry the oxide.

EXPERIMENT 265. To prepare iron rust from ferric chloride. Dissolve 3 or 4 grams of ferric chloride in water, add a slight excess of alkali, as in the previous experiment, collect, wash, dry, and ignite the precipitate strongly. The following changes occur in the process:—



All insoluble hydroxides may be prepared by the method of precipitation.

345. Making metallic oxides by direct oxidation. **EXPERIMENT 266.** 1. Take a bundle of rather fine iron wires, tip them with sulphur, ignite the sulphur, and whilst it burns plunge the wires

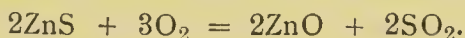
into a jar containing oxygen standing over a little water. The iron will ignite and drops of molten iron oxide will fall into the water.

The forming of rust on iron might be cited as a case of direct oxidation, but it is said that iron only rusts in air which contains carbon dioxide and water vapour, and that the formation of the rust (Fe_2O_3) is preceded by the production of ferric carbonate, which afterwards breaks up into iron rust and carbon dioxide.

2. *The direct formation of oxide of lead.* Melt some lead in a crucible, or in an iron ladle, and stir it well with a rod. The lead will gradually become covered with an earthy substance or dross. This is oxide of lead. Litharge (PbO) and red oxide of lead (Pb_3O_4) are extensively prepared by heating the metal in air.

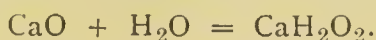
3. *To make 10 grams of oxide of copper (CuO) by direct oxidation.* Heat copper turnings in a hard-glass tube, and draw air over it plentifully. The metal will soon acquire a crust of black oxide of copper, and ultimately the whole of it may be oxidized. This is an excellent method of making oxide of copper.

Oxides are sometimes made by burning metallic sulphides. Thus iron pyrites (FeS_2) is burnt in the making of sulphuric acid (194), and zinc sulphide (ZnS) is burnt in air to convert it into the oxide (ZnO), in the process of extracting this metal from its ore (see 407):—



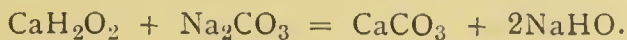
346. Hydroxides. The hydroxides of many metals may be prepared by adding soda to solutions of their salts (see above, Expts. 264 and 265). But those of sodium, potassium, barium, calcium and strontium, which are more or less soluble, cannot be prepared in this way.

EXPERIMENT 267. **To make calcium hydroxide from quicklime.** Place a lump of well-burnt quicklime in a dish, and throw its own weight of water upon it in small quantities at a time. In a little while the lime will become hot, cracks will show themselves in the masses, and soon the whole will fall into an almost white powder. This is calcium hydroxide, or slaked lime (CaH_2O_2):—



Baryta (BaO) and strontia (SrO) behave somewhat similarly.

EXPERIMENT 268. **To make sodium hydroxide.** This substance is formed when sodium is dissolved in water; but it is usually prepared by the action of calcium hydroxide on a solution of sodium carbonate:—



Dissolve 10 or 12 grams of sodium carbonate in some water, add considerable excess of good slaked lime, place the mixture in a well-closed bottle, and warm it, shaking frequently, until the solution no longer effervesces with acid, that is to say, until all the carbonate of soda has been destroyed. Allow the excess of lime and the calcium carbonate to settle, decant the liquid and evaporate it in an iron or, better, in a silver basin. The residue, when cold, will consist of a white, deliquescent solid, which is highly caustic, and which, if pure, does not effervesce with acids.

If you pour some acid on the sediment from which the caustic liquor has been decanted, much carbon dioxide will be given off.

CHAPTER XXIV

THE METALS OF GROUP I. AMMONIUM

347. In the table on p. 181, lithium, sodium, potassium, copper, rubidium, silver, caesium, and gold make up the members of Group I.

The propriety of associating copper, silver, and gold with sodium and potassium may be doubtful, but the other five elements afford a good example of the resemblances that occur among the members of a given group.

Hitherto we have studied the members of the various groups of elements individually, and then compared them with each other, but now the student has gained an elementary idea of the scope of the periodic law, the order of procedure may be altered. If the properties of one or two elements in a given group are known, they may give us a clue to those of the other members of the group. Thus, we have already learnt that sodium and potassium are soft metallic solids which rapidly tarnish in damp air, and dissolve in cold water, expelling hydrogen. Also that they form very alkaline solutions, and combine eagerly with chlorine. Therefore we may expect to find that lithium, caesium, and rubidium, which are members of the same group, exhibit similar properties in a greater or less degree. In future, the student will do well to begin the study of each group by mastering the characters of one of its most important members, afterwards noting very carefully the points in which the other members of the group

resemble, or differ from, this typical element. If this course be followed, he will not only learn the properties of the elements and of their compounds, but also acquire a power of comparing facts, and weighing evidence, which will more than compensate for the extra labour.

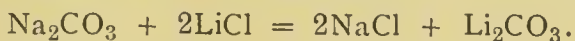
LITHIUM (Li): Atomic weight, 6.98.

348. Lithium is widely spread in nature, but it is not found in large quantities. The best source of supply is said to be the water of Wheal Clifford, in Cornwall, and the element occurs as silicate in several minerals.

Metallic lithium may be obtained by electrolyzing the fused chloride. The metal is rather difficult to make on the small scale, but as it can be purchased, a fragment may be examined. It will be found to be a soft white metal, which quickly tarnishes in air, and attacks water. It melts at 180° and is the lightest metal known, its density being 0.59.

EXPERIMENT 269. Some properties of lithium and its compounds. Hold a drop of a solution of lithium chloride (LiCl) on a platinum wire in the Bunsen flame. Notice that it imparts a crimson colour to the flame. If possible, examine the flame with a spectroscope (336). You will see bright lines in the red and orange.

Add a drop or two of strong solution of carbonate of soda or potash to a little concentrated solution of lithium chloride; a precipitate will fall which will neutralize acids, giving off carbon dioxide. It is therefore a carbonate. A little of the precipitate dissolved in hydrochloric acid will give the characteristic lithium colouration to a flame. It is therefore carbonate of lithium (Li_2CO_3), which, as the experiment shows, is less soluble than the carbonates of sodium and potassium. The following equation explains its formation:—



Lithium hydroxide (LiHO) and lithium phosphate ($\text{Li}_3\text{PO}_4, \text{H}_2\text{O}$) are also rather sparingly soluble.

No crystalline alum, such as those which are formed by potassium, caesium, and rubidium (see 201), has been obtained from lithium.

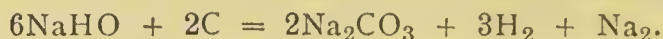
The 'lithia water' of pharmacy is a solution of carbonate of lithium in water containing carbon dioxide.

SODIUM (Na): Atomic weight, 22.88.

349. Compounds of sodium are very widely spread in nature. Its chloride (NaCl) is plentiful both in the sea, and as rock salt, which often occurs in beds of great thickness.

350. Metallic sodium. This metal was discovered by Davy; it is chiefly made from the hydroxide (NaHO).

1. Caustic soda (NaHO) intimately mixed with carbon and metallic iron* is heated strongly in steel retorts. Sodium is liberated and distils away. The following equation is said to represent the change:—



2. Fused sodium hydroxide is decomposed by means of an electric current. The apparatus is so arranged that the hydrogen liberated with the sodium at the kathode protects the latter from oxidation as it floats on the surface of the fused hydroxide, from which it is afterwards removed by a perforated ladle. The temperature of the sodium hydroxide should not be more than 20° above its melting-point.

Sodium is a soft metal which melts at 97.6°. Its density is 0.974. It forms an alloy with potassium which is liquid at ordinary temperatures.

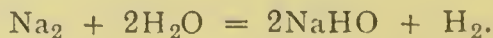
351. Sodium chloride. Common salt (Na Cl). Salt is obtained in many countries by evaporating sea-water, and it was formerly made in this way in Great Britain. It is now largely obtained from deposits of 'rock salt' in the solid state, or in solution from 'brine springs.' The latter are formed by sinking wells in the salt beds and adding water, if necessary. The brine is pumped up, strained and evaporated in open pans. The product often contains small quantities of impurities.

EXPERIMENT 270. **To purify common salt.** Mix a saturated solution of common salt with twice its volume of strong solution of hydrochloric acid. Drain the precipitated salt, wash it with strong solution of hydrochloric acid, and dry it over a flame.

Pure salt is not deliquescent. It crystallizes in cubes. We have already seen that it is about equally soluble in hot and cold water (34).

352. Sodium monoxide (Na₂O). This is a basic oxide (112). It is said to be made by heating sodium in nearly dry air to a temperature not exceeding 180°, but its existence seems doubtful.

353. Sodium hydroxide. Caustic soda (NaHO). This very important caustic alkali is formed when metallic sodium is dissolved in water:—



It is usually made by treating a dilute solution of sodium carbonate with slaked lime (see Expt. 268), or by the electrolysis of solutions of common salt (138, 5). Caustic soda is a white, fusible, very hygroscopic solid, and is soluble in alcohol. It is very alkaline

* Or possibly with a carbide of iron.

to litmus, neutralizes acids, and in the presence of moisture it absorbs carbon dioxide and other acid gases with avidity. It corrodes the skin and other animal matter. It is used in great quantities for making soap, and also by paper-makers. Like all alkalis, soda liberates ammonia from salts of ammonium, and precipitates the hydroxides of many metals from solutions of their salts.

354. Sodium dioxide (Na_2O_2) is a basic peroxide (120). It is made by heating sodium or the monoxide in dried air for some time. It is soluble in cold water, but if the solution be heated it evolves oxygen, and yields a solution of caustic soda. It may be distinguished from the lower oxide by its action with strong hydrochloric acid. When it is warmed with a solution containing a salt of chromium it yields a yellow solution containing sodium chromate; the monoxide, under similar circumstances, gives a green precipitate of hydroxide of chromium or, if added in excess, a fine green solution.

355. Sodium hydride (Na_4H_2) is a light solid of metallic appearance. It is formed by the direct combination of hydrogen with fused sodium at about 350° .

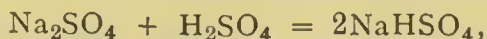
356. Sodium sulphides and sulphates. Under suitable conditions sodium hydrosulphide can be obtained by the action of hydrogen sulphide on soda, and other sulphides, e.g. Na_2S , Na_2S_2 , also exist.

Sodium sulphate (Na_2SO_4) (see also salt-cake, 357).

The hydrated salt (Glauber's salt $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) behaves curiously when warmed with water. Its solubility increases with the temperature employed up to 34° , but a saturated solution of the salt made at 34° deposits its salt gradually if further heated until the temperature reaches about 140° , at which point the deposited salt gradually redissolves (see 33).

For other salts which behave somewhat similarly see calcium sulphate (385) and magnesium phosphate (406).

Sodium hydrogen sulphate (NaHSO_4). To make this salt, add to some sodium sulphate the calculated amount of oil of vitriol—



and evaporate the product, taking care not to overheat the salt (see also 114).

Sodium thiosulphate. See 205.

Sodium nitrate. See 225.

Sodium phosphates. See 259.

Borax and sodium borate. See 318.

Sodium silicate or 'soluble glass.' See 307.

357. Sodium carbonate. The normal carbonate of soda, or disodic carbonate, is prepared in the form of fine decahydrated crystals, known as *soda-crystals* ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), and also in the anhydrous form as *soda-ash* (Na_2CO_3). It is plentiful in the ashes of many seaweeds, and was formerly obtained from this source. It is now manufactured on an immense scale from salt.

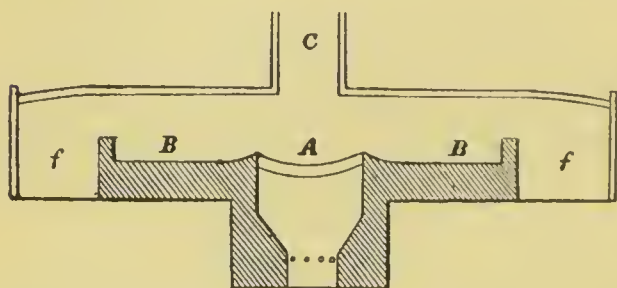
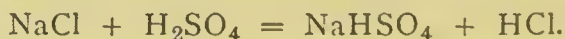


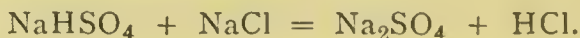
Fig. 131.

The Leblanc process, which has been in use for about a century, is still employed on a very large scale. It is carried out in two stages, called respectively the 'salt-cake' process, and the 'soda-ash' or 'black-ash' process.

1. *The salt-cake process.* In this process equivalent proportions of salt and strong sulphuric acid are moderately heated in a basin *A* (Fig. 131). Acid sodium sulphate is formed, but half the salt remains:—



The mixture of acid sodium sulphate and salt is then raked to the floors *B B*, where it is more strongly heated by flames from the furnaces *f f*, and converted into salt-cake:—



The hydrochloric acid produced in these operations is carried off by the flue *C* and dissolved in water, or else is mixed with air and used at once for making chlorine by Deacon's process (138, 4).

Salt-cake may also be made by exposing salt to sulphur dioxide (made from pyrites), air, and steam at 500° .

2. *The black-ash process.* Salt-cake, small coal, and limestone in suitable proportions are well mixed and heated strongly in a black-ash furnace (Fig. 132).

This consists of a cylindrical iron drum, which can be rotated about its axis, and which stands between a furnace at *B* and a flue at *C*. The furnace is lined with firebricks, and is capable of receiving a charge

of several tons. After it has been charged the furnace is rotated by a small engine, whilst its contents are heated by flames which enter the furnace from a fire at *B*.

The spent gases pass away by *C*, and, as they are very hot, are used to evaporate solutions containing alkali on their way to the flue by which they ultimately escape. When the charge has been sufficiently heated *D* is opened, and the contents of the furnace are run off into moulds and allowed to cool. The product, 'black-ash,' consists chiefly of calcium sulphide and sodium carbonate, formed, it is supposed, by the following reaction :—

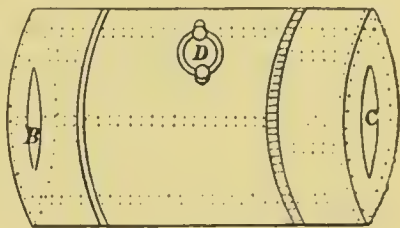


Fig. 132.

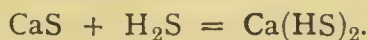


But some of the limestone (CaCO_3) is converted into quicklime (CaO), and the black-ash usually also contains some unaltered coal, salt, sodium sulphate, &c., and carbon monoxide is also formed.

The black-ash is treated with water. This dissolves the carbonate of soda, together with some sodium hydroxide, formed at its expense by the action of the lime (353), and other impurities. The solution is boiled down, and deposits the carbonate as 'soda-salt,' which is calcined to form 'soda-ash' (Na_2CO_3). The soda-ash may be redissolved and crystallized for the production of 'soda-crystals' ($\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$).

The mother liquors, which contain carbonate of soda and also some sodium hydroxide, are treated with lime, strained and concentrated to produce caustic soda (NaHO).

The sulphur in the calcium sulphide (*soda-waste*), which remains undissolved, is, as far as possible, recovered, and reconverted into sulphuric acid, or into sulphur. For this purpose the waste is treated with carbon dioxide in the presence of water; the hydrogen sulphide liberated is passed into vessels containing more of the waste, which it converts into hydrosulphide :—



This also is treated afterwards with carbon dioxide, and the hydrogen sulphide thus produced is converted into sulphur dioxide, which can be made use of in the vitriol chambers (194).

Elementary sulphur may also be made from the hydrogen sulphide.

To obtain this, the sulphide, mixed with sufficient air, is conducted to a chamber containing warm ferric oxide. Partial oxidation of the sulphide takes place, water being formed and sulphur liberated. The latter is condensed in suitable chambers.

The ammonia-soda process. This process was introduced much later than that of Nicholas Leblanc. It consists, essentially, in saturating brine with ammonia at a low temperature, after removing the calcium and magnesium usually present in salt, and then adding carbon dioxide under slight pressure. Sodium bicarbonate (NaHCO_3) and ammonium chloride (NH_4Cl) are formed:—



and the former is deposited from the solution owing to its comparatively moderate solubility in water.

The carbon dioxide is generated from limestone or magnesite, together with a corresponding amount of lime, or magnesia, which can be employed to liberate the ammonia of the ammonium chloride so that it becomes available for further use (Expt. 161).

The bicarbonate of soda is heated to convert it into the carbonate:—



and the carbon dioxide thus set free becomes available for further use. Thus, in the ammonia-soda process, salt, limestone (or magnesite), and ammonia are used, and sodium hydrogen carbonate, calcium chloride, and ammonia are produced in the course of each cycle of operations. The first of these is sold, the last can be used again, and it is said that part of the chlorine can be recovered and made useful. The ammonia-soda process has the advantage of being comparatively simple, and it requires a smaller consumption of fuel than its rival. The crude product, moreover, requires less purification than that made by the Leblanc process. On the other hand it is doubtful whether hydrochloric acid and chlorine can be so advantageously produced by this method, as in the older process.

The student will gain some idea of the importance of the soda industry, when it is mentioned that about 800,000 tons of salt are converted into alkali annually in Great Britain.

EXPERIMENT 271. The properties of sodium carbonate.

1. Add some soda crystals to some water; notice that they readily dissolve, giving an alkaline solution. All other carbonates, except those of metals of the alkalis, are insoluble.

2. Boil some solution of sodium carbonate, and examine the action

of the steam on lime-water. No carbon dioxide will be detected (see bicarbonates, 281).

3. Heat some dry carbonate of soda to a bright red heat in an open crucible and allow it to cool; then pour acid upon it. Notice that it still effervesces, giving off carbon dioxide plentifully. Only the carbonates of the metals of the alkalis remain undecomposed when thus strongly heated with free access of air.

4. Powder a fresh clean crystal of soda and, after weighing it, expose it to the air in a warm dry room for some days. Notice that it becomes efflorescent, and gradually decreases in weight owing to the loss of its water of crystallization.

358. Sodium hydrogen carbonate or bicarbonate of soda. We have seen that if carbon dioxide be passed through a cold saturated solution of potassium carbonate, it yields a white solid, less soluble than the normal carbonate (281). This is potassium hydrogen carbonate:—



and sodium hydrogen carbonate may be made by a similar process.

Repeat Experiment 271, using sodium bicarbonate. You will find that it is soluble, alkaline, and evolves carbon dioxide with acids. When you heat the dry salt, or its solution, carbon dioxide will be given off:—



Sodium is distinguished by the solubility of its salts, by the soluble, alkaline character of its oxide and carbonate, by the yellow tinge which many of its compounds give to a flame, by the characteristic yellow line present in the spectrum of a sodium flame, and by the solubility of sodium hydrogen tartrate.

POTASSIUM (K): Atomic weight, 38.86.

359. Potassium and sodium were discovered at about the same time by Sir Humphry Davy (1807), who obtained them in very small

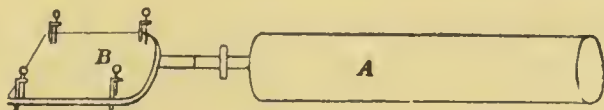
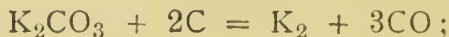


Fig. 133.

quantities, by the electrolysis of moist potash and soda. The former metal was made, for many years, by strongly heating carbonate

of potassium with carbon in a retort *A* (Fig. 133), connected with a covered tray *B*, which was kept cool by means of a moistened cloth and acted as a condenser. The principal reaction may be written :—



but a process resembling that described in 350 is now frequently substituted for the older method. Crude potassium and sodium may be purified by redistilling them *in vacuo* or in nitrogen.

Potassium is a white or slightly pink, soft metal, which tarnishes quickly in air. [Why?] Its density is 0.87. It melts at 62°, and volatilizes at a low red heat. If a few grams of potassium are melted at one end of an exhausted tube and allowed to cool slowly, crystals will form, which may be detected by decanting the still fluid part of the metal before the whole has solidified. Potassium reacts with water even more violently than sodium, and combines readily with the more active non-metals, such as oxygen and chlorine.

The ashes of land plants contain carbonate of potassium, which may be extracted with water, and these ashes were formerly the chief source of potassium and its salts, but large supplies of potash salts are now obtained from deposits of *carnallite* ($\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$) and *syilvine* (KCl), which occur, intermixed with other minerals, at Stassfurt.

Potassium forms several oxides, viz. a basic monoxide (K_2O), which is said to be formed by heating the tetroxide to redness, and which corresponds to the hydroxide; a *dioxide* (K_2O_2), and a *tetroxide* (K_2O_4). The last is a pale-yellow solid. It is formed when potassium is burnt in excess of oxygen, and acts like a peroxide (120); when treated with water it gives off oxygen.

Potassium hydride (K_4H_2) is formed by direct combination at 400°. It is a brittle, crystalline substance, which exhibits metallic lustre. It may be decomposed by heating it in a vacuum.

360. Potassium hydroxide or caustic potash (KHO).

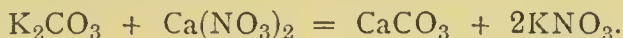
This compound closely resembles sodium hydroxide, and may be prepared in a similar manner (Expt. 268).

361. Potassium sulphate (K_2SO_4). This salt is left in the retorts when nitric acid is made from nitre (KNO_3) (225). Its crystals are anhydrous (compare sodium sulphate, 356). It is more soluble in hot than in cold water. There is also an acid sulphate of potassium (KHSO_4), which is very soluble, and exhibits the characteristic reactions of an acid salt (114).

362. Potassium nitrate, nitre (KNO_3). Nitrification.

Nitre is found as an incrustation on the soil in hot countries. It is produced, through the agency of certain micro-organisms, from nitrogenous organic matter. One of these organisms generates nitrites from ammonia (see 217); the second converts nitrites into nitrates. The two organisms in question are present in all fertile soil, and help to render the nitrogenous substances applied to the soil available for the nourishment of plants.

In hot countries, where nitrification proceeds rapidly, nitre is extracted from the soil by lixiviating it with water. In Europe it is prepared artificially by exposing heaps of animal refuse mixed with slaked lime and garden soil. The heaps are protected from rain, but exposed to the air, and they are treated at intervals with further supplies of nitrogenous matter in a liquid form. Calcium nitrate is produced. This is extracted from the mass by means of water, and the solution thus obtained is mixed with carbonate of potassium, when the following change occurs :—



The calcium carbonate falls as a precipitate, and the nitre is obtained by evaporating the solution.

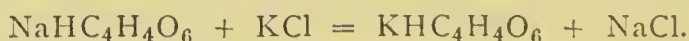
Nitre may also be made by dissolving equivalent proportions of nitrate of soda (Chili saltpetre) and chloride of potassium in water, and concentrating the solution. As the water evaporates, sodium chloride separates, leaving the solution enriched with nitre. The latter salt, which is more soluble in hot water than in cold, is obtained by cooling the mother liquor, after much of the common salt has been removed.

Like other nitrates, nitre yields nitric acid, when heated with oil of vitriol (see 225). It is soluble in its own weight of hot water, and is deposited from aqueous solutions in crystals. Large quantities of nitre are consumed for making gunpowder (230). Fused nitre is a powerful oxidizer; it converts carbon into carbon dioxide, and sulphur into a sulphate, as shown in Experiment 174, and it is used extensively by makers of fireworks.

363. Carbonate of potassium. The normal carbonate of potassium (K_2CO_3) is present in the ashes of vegetable matter, and may be extracted from the ashes of wood. It may also be made by igniting the potassium salts of vegetable acids.

EXPERIMENT 272. To prepare potassium carbonate. Heat a few grams of the acid tartrate of potassium strongly in a crucible; extract the carbonaceous residue with boiling water; filter and evaporate the solution. A white alkaline salt will remain which gives the reactions of potassium (see below), and evolves carbon dioxide when added to an acid. This salt is carbonate of potassium (K_2CO_3).

Potassium carbonate may be prepared from the chloride by a modification of the Leblanc process. It is powerfully hygroscopic and easily soluble in water, alkaline to litmus, and neutralizes acids, but it is not decomposed by heat. If it be acidulated with hydrochloric acid it gives a lilac colour to the Bunsen flame, and if neutralized, and then mixed with a concentrated solution of sodium acid tartrate ($NaHC_4H_4O_6$), it gives a precipitate of the comparatively insoluble acid tartrate of potassium ($KHC_4H_4O_6$):—



364. Potassium and hydrogen carbonate. If you pass a stream of carbon dioxide through a saturated solution of the normal carbonate, crystals of the acid carbonate will be deposited (see Expt. 216):—

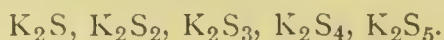


If Experiment 271 be repeated with this salt, the results obtained will be similar to those afforded by the corresponding salt of sodium, from which it may be distinguished, however, by the different character of its crystals, and by the above-mentioned tests for potassium.

Bicarbonate of potassium is a much milder alkali than the normal carbonate and consequently is more suitable for internal administration.

365. Potassium and hydrogen tartrate ($KHC_4H_4O_6$). This salt is deposited from grape juice during fermentation, owing to the fact that it is less soluble in solutions containing alcohol than in water.

366. Potassium sulphides. These form a series of compounds which are said to correspond to the formulæ:—



There is also a hydrosulphide (KHS). The latter can be obtained in colourless crystals having the composition $2KHS, H_2O$ by adding hydrogen sulphide to solution of potassium hydroxide and concentrating *in vacuo*. When its solution is exposed to the air it turns yellow, owing, it is said, to the formation of potassium disulphide (K_2S_2).

367. Potassium iodide (KI). This salt is much used in medicine. It is most economically prepared by adding iodine to solution of potassium hydroxide :—



strongly heating the mixture of iodate (KIO_3) and iodide of potassium, either alone or with carbon, to reduce the iodate, and crystallizing the product from water. Potassium iodide crystallizes in cubes; it is readily soluble in water and alcohol, and its solution is an excellent solvent for iodine (see 165).

368. Potassium bromide (KBr) is also a valuable medicinal agent. It is prepared by adding bromine to solution of potash, and igniting the product; both this salt and the iodide are decomposed by chlorine (163).

369. Potassium alum has already been mentioned in 201.

Potassium chlorate. See 151.

Potassium perchlorate. See 153.

Several of the characteristic properties of salts of potassium have already been mentioned in 363. Compounds of potassium may be distinguished from those of sodium by the characteristic double chloride ($\text{PtCl}_4, 2\text{KCl}$) which is formed when a little platinic chloride is added to a solution containing chloride of potassium, by the slight solubility of the silicofluoride of potassium, and by the characteristic spectra of the two metals.

RUBIDIUM (Rb) : Atomic weight, 84.8. CÆSIUM (Cs) : Atomic weight, 131.9.

370. These two rare metals were discovered by Bunsen, by the aid of the spectroscope, in the waters of the Dürkheim springs. They both occur in lepidolites, in some other silicates and in the ashes of several plants.

Both these metals form double salts with platinum chloride of the type $\text{PtCl}_4, 2\text{MCl}$; they are less soluble than the corresponding potassium salt, and may be used to separate caesium and rubidium from potassium. Both form powerfully alkaline hydroxides and soluble carbonates. Both also form alums (see 201), that of rubidium being more soluble in water than the corresponding caesium salt.

The metals are silver-white, and are isolated with difficulty. Both decompose cold water. Caesium melts at about 26° , and rubidium has

also a very low melting-point, 38.5° . They are both heavier than water. Many of their salts are isomorphous with those of potassium, and their spectra exhibit several characteristic lines by which they may be identified. They may be separated by taking advantage of the fact that caesium tartrate is much more soluble than tartrate of rubidium.

SALTS OF AMMONIUM.

371. It has been stated already that ammonia (NH_3) combines with acids yielding salts in which the radicle (NH_4) may be considered to replace an atom of potassium in the salts of that metal. Ammonium has not been isolated, but a soft, pasty, metallic mass which is formed when sodium amalgam is placed in a saturated solution of sal-ammoniac has been supposed to contain ammonium amalgam. It is very doubtful whether the substance in question is a true amalgam.

As the chemistry of ammonia has already been studied, it will be sufficient to give a brief account of some of the most important salts of ammonium.

372. Ammonium chloride or sal-ammoniac (NH_4Cl). This salt may be made by neutralizing solution of ammonia with hydrochloric acid. It is prepared in large quantities from the ammoniacal liquor of gasworks by heating it with lime to expel the ammonia, and passing this into solution of hydrochloric acid. The salt then separates from the liquid in crystals, which are drained and dried.

Ammonium chloride has a sharp saline taste, and it is freely soluble in water. When heated strongly, it dissociates (see 198, 220):—



but as the products recombine on cooling, it can nevertheless be sublimed in closed vessels.

It is extensively used as a source of ammonia (217), and forms a double salt $2(\text{NH}_4)\text{Cl}, \text{PtCl}_4$ which is isomorphous with the corresponding salt of potassium.

373. Ammonium nitrate. This salt may be made from ammonia and nitric acid. It is soluble, and crystallizes in six-sided prisms.

When heated, it yields nitrous oxide and water (see 240):—

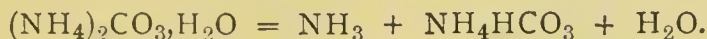


If strongly heated it is apt to give rise to explosions owing to the instable character of nitrous oxide.

Ammonium nitrite. See nitrogen (213, 4).

374. Ammonium sulphate. Forms a well defined alum (see 201).

375. Ammonium carbonates. Several carbonates of ammonium are known, e.g. a *normal carbonate* $((\text{NH}_4)_2\text{CO}_3, \text{H}_2\text{O})$, which is made by adding ammonia to the acid salt. It readily parts with ammonia, forming the acid salt:—



An acid carbonate or *bicarbonate* may be made by saturating solution of ammonia with carbon dioxide. It is one of the constituents of guano. The carbonate of ammonium of commerce when freshly made consists of a mixture of the bicarbonate with a salt known as carbamate of ammonium $((\text{NH}_4)(\text{NH}_2)\text{CO}_2)$. It is made by heating together sal-ammoniac and chalk (CaCO_3) .

If a small fragment of the freshly made ammonium carbonate of commerce is dissolved in cold water, and mixed with a little solution of ammonia and excess of calcium chloride, it will give a plentiful precipitate of calcium carbonate. If the filtered solution be then warmed, the carbamate present will take up water, and a further precipitate of calcium carbonate will fall.

376. Ammonium hydrosulphide (NH_4HS) is made by saturating ammonia solution with hydrogen sulphide. The solution becomes yellow by exposure. It is largely used as a reagent.

377. Ammonium phosphates. Several salts of ammonium with phosphoric acid are known. When these are heated they lose ammonia and water, and leave residues of metaphosphoric acid.

Microcosmic salt $(\text{NH}_4\text{NaHPO}_4, 4\text{H}_2\text{O})$ is described in 259.

378. The metallic derivatives of ammonium. A number of compounds are known which may be considered to be compounds of ammonium (NH_4) in which the hydrogen has been partly replaced by metals. Thus, when ammonia is added to a solution of mercuric chloride (HgCl_2) , a precipitate falls which may be supposed, from its mode of formation and composition, to be mercurammonium chloride $(\text{NH}_2\text{Hg}''\text{Cl})$; and a similar compound having the formula $\text{N}_2\text{H}_6\text{Hg}''\text{Cl}_2$ is obtained by dropping a solution of the mercury salt into a boiling solution containing sal-ammoniac and ammonia. Again, dry calomel when exposed to ammonia gas yields mercuroso-

ammonium chloride ($\text{N}_2\text{H}_6(\text{Hg}_2)''\text{Cl}_2$), and the same salt when digested in ammonia solution forms dimercuroso-ammonium chloride ($\text{NH}_2(\text{Hg}_2)''\text{Cl}$). Another compound belonging to the same class is the sulphate of cuprammonium ($\text{N}_2\text{H}_6\text{Cu}''\text{SO}_4$).

CHAPTER XXV

CALCIUM, STRONTIUM, AND BARIUM

THE oxides of calcium, strontium, barium, and magnesium were formerly known as the 'alkaline earths,' but magnesium is more nearly related to zinc and cadmium than to the above three metals, as will presently be understood. In the table on p. 181 the three metals now under consideration are even series members of Group II; whilst magnesium, zinc, cadmium, and mercury are the odd series members of the same group.

Calcium, barium, and strontium were first obtained by Sir Humphry Davy by electrolysis. Calcium and strontium have usually been described as yellow metals. The former, however, is really white, and barium is also a white metal. They are all denser than water, they are all tarnished by damp air, and decompose water readily at ordinary temperatures. They all form insoluble carbonates, which are decomposed by heat, and their oxides are soluble, though less so than the oxides of metals of Group I, and alkaline.

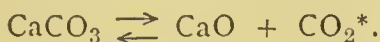
CALCIUM (Ca): Atomic weight, 39.8.

379. Compounds of this metal are very abundant, but it is never found free. It is now prepared on a comparatively large scale by electrolysing the chloride, and specimens can be obtained from dealers in chemicals.

It occurs as carbonate (CaCO_3) in the various limestones, and in dolomite or magnesian limestone, which consists of the carbonates of magnesium and calcium; as sulphate in *gypsum* and *selenite*; as fluoride (CaF_2) in *fluor-spar*; and bones are composed largely of calcium phosphate. The most important compounds of calcium are the following:—

380. Calcium oxide, quicklime (CaO). This is best obtained by igniting pure calcium carbonate (Expt. 261). Quicklime is made on the large scale by heating limestone in a lime-kiln (Fig. 134).

In structure a lime-kiln is not altogether unlike a 'blast furnace,' but the former is usually much smaller than the latter, and is less expanded at its middle. A mixture of limestone and coal is usually fed into the kiln at *A*. The burning of the coal with the air drawn in from below produces the heat necessary to decompose the limestone:—



The gaseous products of the change escape, mixed with nitrogen and carbon monoxide, from the mouth of the kiln, whilst the lime falls, and is gradually withdrawn at *B*.

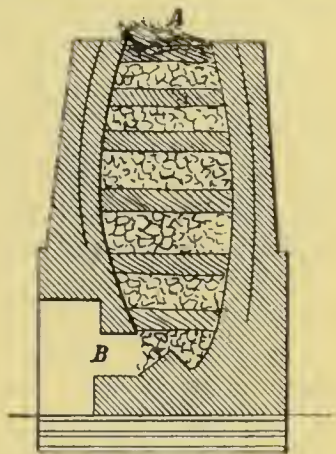


Fig. 134.

Great quantities of lime are used in the manufacture of mortar and cements. It promotes the decay of vegetable matter, becoming itself reconverted into carbonate in the process, and therefore is useful on land where vegetable matter is in excess. It is also useful to chemists, and in the chemical arts; for example, it is used in the making of caustic soda and potash (Expt. 268), for absorbing acid gases such as carbon dioxide and hydrogen sulphide (see 303), and the tanner loosens the hair on hides by its aid.

Mortar is a mixture of lime and sand with water. It hardens partly by drying, to some extent through the gradual forming of calcium carbonate, and partly also in consequence of the forming of calcium silicate, but all mortar, however old, is said to contain some uncombined lime.

Hydraulic cements are made from limestones in which calcium carbonate is associated with a moderate proportion of clay, or by calcining mixtures of prepared chalk with clay. These cements, which may be regarded as basic silicates, 'set' when mixed with water, and the hardened material is not afterwards disintegrated by immersion in water, as common mortar would be. The cause of the 'setting' of cements is not thoroughly understood, but very possibly the water and cement unite to form a hydrated and insoluble silicate of calcium and aluminium.

* If limestone is heated in a closed vessel the decomposition is incomplete, as the lime and carbon dioxide recombine on cooling.

Lime, as we learnt from Experiment 261, is a hard, nearly white solid, which will absorb considerable quantities of water, evolving much heat and forming calcium hydroxide, or *slaked lime* (CaH_2O_2). It emits a very intense white light when strongly heated.

381. Calcium hydroxide or slaked lime (CaH_2O_2) (346). This is the form in which lime is chiefly used. Quicklime is employed for drying ammonia, but it is slaked before it is used for most of the purposes mentioned above. Slaked lime is reconverted into quicklime if it be strongly heated:—



It is slightly soluble in water, and rather more soluble in cold water than in hot. Its aqueous solution, *lime-water*, is alkaline to litmus, neutralizes acids, liberates ammonia from its salts (217), and is used as a test for carbon dioxide.

There is a *dioxide of calcium* (CaO_2) which resembles the corresponding oxide of barium, but it is not produced by the direct combination of lime and oxygen.

382. Calcium fluoride, fluor-spar (CaF_2). This beautiful mineral is found in fine crystals, which often accompany lead ores, and which exhibit a variety of colours. The crystals are usually cubic or octahedral, and some varieties, when hot, emit a pale phosphorescent light, which may be easily seen in a dark room. An account of its composition and of its use as a source of hydrofluoric acid will be found in 171.

383. Calcium chloride (CaCl_2) is chiefly obtained as a by-product in making carbon dioxide (279), or in preparing ammonia by warming sal-ammoniac (NH_4Cl) with slaked lime (Expt. 161).

EXPERIMENT 273. The properties of calcium chloride. Dissolve some calcium chloride in a little water and evaporate the solution to a syrup. Allow this to cool in a dessicator. It will presently deposit crystals corresponding to the formula $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Evaporate another portion of the solution to dryness, and heat the residue strongly. You will obtain a porous mass which contains much less water, and which, owing to its hygroscopic character, is useful for drying gases. Expose a few fragments of the residue to the air. It will gradually become damp, and will ultimately liquefy. If this liquid be distilled, water and a residue of dry calcium chloride will be obtained from it.

Calcium bromide and iodide (379) are known.

384. Calcium carbonate or limestone (chalk, marble, coral, pearl, &c.) (CaCO_3). Calcium carbonate is plentiful in almost all parts of the world. It occurs finely crystallized as *calc-spar* or *Iceland spar*, which has the density 2.7, and in the form of *arragonite*, the density of which is about 3.0*.

It has been observed that the minute crystals of calcium carbonate produced by mixing a cold solution of an alkaline carbonate with one containing a salt of calcium resemble calc-spar, but that if the same substances be mixed at 90° , the precipitate consists chiefly of crystals resembling arragonite. Calcium carbonate is frequently of animal origin. Thus it is the chief component of the egg-shells of birds, of the shells of molluscs, and of coral, chalk and oolite.

As we have previously learnt, limestone is our chief source of lime and carbon dioxide. It is almost insoluble in pure water, but is distinctly soluble in water containing carbon dioxide. Its presence in water causes *temporary hardness*, and hard waters contribute to the forming of stalactites and stalagmites (11).

385. Calcium sulphate (CaSO_4). The native salt, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, occurs in masses as *gypsum* and *alabaster*, and in single crystals, which are often of considerable size, as *selenite*.

Only one part of calcium sulphate will dissolve in about 450 parts of water, but it is more soluble in the presence of sodium chloride. At temperatures above 35° its solubility diminishes. It is one of the salts which cause the permanent hardness of water (see 11).

Plaster of Paris is made from the native hydrated calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), by heating it for some time to about 130° . This treatment expels a great part of its water of crystallization. If some of the salt, thus partly dried, be made into a paste with water, the mixture soon 'sets,' that is, becomes solid, owing to the salt recombining with water.

Parian cement, which is harder when dry than plaster of Paris, is made by heating sulphate of calcium with a suitable proportion of borax.

386. Calcium phosphates. These important compounds yield a great part of our phosphorus. *Tricalcic phosphate* ($\text{Ca}_3\text{P}_2\text{O}_8$) is present in the mineral *apatite*, and is the chief mineral component of bones and coprolites. It may be prepared, as a precipitate, by mixing

* When a substance exhibits two distinct crystalline forms, it is said to be *dimorphous*.

sodium phosphate with a solution of calcium chloride to which ammonia has previously been added.

Calcium tetrahydrogen phosphate ($\text{CaH}_4\text{2PO}_4$) can be obtained in crystals by dissolving tricalcic phosphate in a solution of phosphoric acid, and allowing the product to evaporate over oil of vitriol in a dessicator :—



Superphosphate of lime. A mixture of monocalcium phosphate and calcium sulphate, prepared by digesting bone-ash, coprolites, &c., with sulphuric acid, is largely used under this name as a manure.

387. Calcium sulphides. *Calcium monosulphide* (CaS) is one of the constituents of black-ash (see 357). It is produced by reducing sulphates by carbon, in the presence of alkalis or alkaline carbonates. *Calcium disulphide* (CaS_2) is one of the products of boiling calcium hydroxide and sulphur with water. It is deposited in hydrated crystals ($\text{CaS}_2, 3\text{H}_2\text{O}$) as the solution cools. (For the action of acids on this salt see 185.) Prolonged boiling with excess of sulphur leads to the formation of a *pentasulphide of calcium* (CaS_5). Calcium thio-sulphate (CaS_2O_3) usually accompanies both the above compounds.

Bleaching powder or chloride of lime. See 150.

Calcium carbide (CaC_2). See 302.

388. Salts of calcium give a slightly soluble precipitate ($\text{CaSO}_4, 2\text{H}_2\text{O}$) with solutions of soluble sulphates. They are not precipitated by potash or soda from dilute solutions, but are precipitated by the alkaline carbonates and oxalates.

When moistened with strong solution of hydrogen chloride, calcium salts give an orange-red colour to the Bunsen flame, and yield a characteristic spectrum.

STRONTIUM (Sr) : Atomic weight, 86.94.

389. The chief sources of this metal are the carbonate *strontianite* and the sulphate, *celestine*. Strontium is said to be a yellow metal, its density is about 2.5, it will burn in air and decomposes cold water.

390. Strontium monoxide or strontia (SrO) is a basic oxide (120). It may be prepared by igniting the carbonate, or nitrate, of

strontium. It forms a hydroxide (SrH_2O_2), which is alkaline, and more soluble than calcium hydroxide. It has been used in extracting sugar from the juice of the beet-root.

Strontium dioxide (SrO_2) is not produced by heating strontia in air (see barium dioxide, 117, 2), but by adding hydrogen peroxide to an aqueous solution of strontia, and drying the precipitate at 100° .

391. Strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$). This salt is much less deliquescent than calcium chloride. It may be made by dissolving oxide or carbonate of strontium in hydrochloric acid.

392. Strontium sulphate (SrSO_4) occurs as *cælestine*. It is less soluble than calcium sulphate (1 in 7000). The crystalline masses of the native salt sometimes exhibit a pale blue colour.

393. Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) is used for making 'red fire.'

394. Strontium carbonate occurs native as *strontianite*, which is isomorphous with arragonite (384).

The salts of strontium give a bright red colour to the Bunsen flame, and their aqueous solutions give precipitates of sulphate when mixed with solutions of calcium sulphate. They are not readily precipitated by potash or soda, but are precipitated by alkaline carbonates. The spectrum of strontium is richer in red lines than that of calcium.

BARIUM (Ba): Atomic weight, 136.4.

395. This metal occurs as *heavy-spar* or *barytes* (BaSO_4) and also as *witherite* (BaCO_3). It is made by electrolyzing the fused chloride in the presence of sal-ammoniac. It is a white metal, which, like strontium, burns in air and decomposes cold water.

396. Barium monoxide or baryta (BaO) is a basic oxide which is prepared by igniting the carbonate or nitrate. Like lime, it combines vigorously with water, forming barium hydroxide ($\text{Ba}(\text{HO})_2$), which is much more freely soluble in water than slaked lime and is more soluble in hot water than in cold. Like other soluble basic oxides it is alkaline to litmus. A solution of baryta affords us a most delicate test for carbon dioxide, as carbonate of barium is very insoluble.

Barium dioxide (BaO_2). For the mode of preparing and uses of this substance see 117, 2.

397. Barium sulphate (BaSO_4). This is found native as *barytes* or *heavy-spar*. It is a dense solid, very insoluble in water and in dilute acids, but somewhat soluble in hot oil of vitriol. Barytes is sometimes used as a substitute for white lead in the manufacture of oil paints. Barium sulphate may be converted into the chloride by fusing it with calcium chloride and a reducing agent, such as carbon or iron, and extracting the barium chloride from the product with hot water.

398. Barium carbonate or witherite (BaCO_3) is found native. It is exceedingly insoluble, and is easily decomposed by heat.

Nitrate of barium ($\text{Ba}(\text{NO}_3)_2$) and **Chloride of barium** ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) are both soluble salts; the chloride is not deliquescent. The nitrate is used by pyrotechnists.

Salts of barium give a green colour to the Bunsen flame*, and exhibit a spectrum which is rich in green bands (see frontispiece). Their solutions yield highly insoluble precipitates when mixed with solutions of soluble sulphates, and are precipitated by silicofluoric acid. Dilute potash and soda do not precipitate baryta from solutions of its salts, but the alkaline carbonates throw down barium carbonate.

CHAPTER XXVI

BERYLLIUM. MAGNESIUM. ZINC. CADMIUM

MAGNESIUM, zinc, and cadmium, like the metals of the alkaline earths, are divalent, volatile at high temperatures, and burn if strongly heated in air or oxygen. They have little action on cold water, but magnesium and zinc attack water at high temperatures. They dissolve in dilute sulphuric or hydrochloric acid, evolving hydrogen. They form basic oxides of the type $\text{M}''\text{O}$, and a corresponding sulphide, but no peroxides. Their oxides, carbonates, and phosphates are practically insoluble (see magnesia, 402, however), but their sulphates dissolve readily in water.

* The sulphate and some others should first be moistened with strong HCl .

These three metals, with mercury, form the odd series members of Group II.

399. Beryllium or glucinum (Be). The remaining member of Group II is a rare element which occurs as silicate in *beryl*, *emerald*, and in some other minerals. It is made by reducing the chloride with sodium. The specific heat of beryllium is 0.62. Its equivalent weight is 4.54; hence its atomic weight is 9.1 (see 95). Beryllium is a white, crystalline, somewhat light metal ($D = 1.85$). It is without action on hot water, but dissolves in hydrochloric acid and in sulphuric acid, and also in potash. Its soluble salts are distinguished by their sweetish taste. Beryllium hydroxide is soluble in potash like alumina, and also in acids, but its oxide does not become blue when ignited with oxide of cobalt.

MAGNESIUM (Mg): Atomic weight, 24.18.

400. This metal is found as carbonate in *magnesite*, is associated with calcium carbonate in *dolomite*; and occurs as silicate in *asbestos*, *talc*, *serpentine*, *steatite*, and *hornblende*. It is present in sea-water, and in certain mineral waters, usually as sulphate or bromide. It is largely extracted from *carnallite*, and is one of the components of bone-ash.

The metal is made by reducing the double chloride of magnesium and potassium, after drying it (see carnallite, 359), with sodium, and redistilling the crude product.

Magnesium burns in air (see Expt. 1), giving an intensely bright flame, which is very rich in the more refrangible rays. It also burns in carbon dioxide (see Expt. 214), and combines directly with nitrogen (see argon, 216). It is not very dense ($D = 1.74$). It melts at a red heat, and is volatile at higher temperatures. It dissolves in acids readily, and displaces copper and silver from solutions of their salts.

401. Magnesium chloride ($MgCl_2 \cdot 6H_2O$) is a very deliquescent crystalline solid. If a solution of this salt be evaporated to dryness, it evolves hydrochloric acid leaving a residue which contains magnesia. The anhydrous salt may be obtained by evaporating its solution after adding an equivalent proportion of ammonium chloride. Magnesium was formerly prepared from the chloride by the action of sodium.

402. Magnesium oxide or magnesia (MgO). EXPERIMENT 274. Heat some carbonate of magnesia to redness in a glass

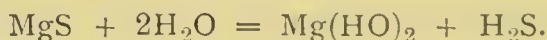
tube, provided with a delivery tube. Notice that carbon dioxide is given off. The residue will consist of *magnesia* (MgO).

Throw a little water on some magnesia. Hydroxide of magnesium ($\text{Mg}(\text{HO})_2$) will be formed, and if it be shaken with water, its solution will turn moist red litmus paper blue.

Its solubility is slight, however, for 55,000 parts of water are said to dissolve only 1 part of magnesia at ordinary temperatures, and it is less soluble in hot water.

If magnesia is warmed with dilute sulphuric acid or with hydrochloric acid, it neutralizes the acid, yielding a salt, but no oxygen or chlorine are evolved. It is therefore a basic oxide.

403. Magnesium sulphide (MgS) is a solid substance which is decomposed by water:—



404. Magnesium sulphate ($\text{MgSO}_4, 7\text{H}_2\text{O}$). This salt occurs in various spring waters and in sea-water. It is known as Epsom salts, and is used in medicine as a purgative.

EXPERIMENT 275. To make Epsom salts from dolomite. Digest some calcined and powdered dolomite in dilute sulphuric acid. Notice that the solid does not dissolve completely. Decant the solution from the less soluble calcium sulphate, evaporate it to a small bulk, and allow it to cool; crystals of Epsom salts ($\text{MgSO}_4, 7\text{H}_2\text{O}$) will be formed. They may contain traces of calcium sulphate.

Magnesium sulphate formerly was made extensively by the above method, but now it is obtained chiefly from *kieserite* ($\text{MgSO}_4, \text{H}_2\text{O}$), which occurs in the salt beds at Stassfurt.

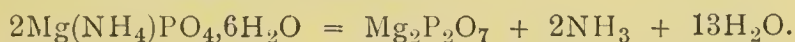
When magnesium sulphate is heated, it readily parts with six molecular proportions of water, and leaves a residue which corresponds to the formula $\text{MgSO}_4, \text{H}_2\text{O}$. If a solution containing molecular proportions of magnesium sulphate and potassium sulphate be concentrated, it deposits crystals, which have the composition $\text{MgSO}_4, \text{K}_2\text{SO}_4, 6\text{H}_2\text{O}$. An analogous salt is formed with ammonium sulphate. These salts may be regarded as heptahydrated magnesium sulphate ($\text{MgSO}_4, 7\text{H}_2\text{O}$), in which a molecular proportion of water is replaced by a molecular proportion of the alkaline sulphate.

405. Magnesium carbonate (MgCO_3) occurs native as magnesite, and is one of the constituents of dolomite. The precipitate formed when an alkaline carbonate is added to solution of

magnesium sulphate is a variable mixture of this substance with magnesium hydroxide.

406. Magnesium phosphates. Trimagnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2$) is present in certain plants and seeds, and it is one of the constituents of bones.

Ammonium and magnesium orthophosphate ($\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is formed when sodium phosphate is added to a solution containing a salt of magnesium together with ammonium chloride and ammonia. Its formation affords us a useful test for magnesium. If this salt be strongly heated, it loses water and ammonia, and yields a residue of magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$):—



The salts of magnesium are not precipitated by ammonium hydroxide, sulphide, or carbonate in the presence of ammonium chloride. They give the above-mentioned precipitate of magnesium and ammonium phosphate when treated with sodium phosphate (see above); and if strongly ignited before the blow-pipe on charcoal they leave an alkaline residue which glows brightly when hot, and becomes pink if it be reheated with nitrate of cobalt.

ZINC (Zn): Atomic weight, 64.9.

407. This metal is extensively used in making 'galvanized iron,' and by chemists for making hydrogen; it is usually associated with cadmium. Its chief ores are *blende* and *calamine*. Blende contains zinc sulphide (ZnS); it is found in various parts of England and the Isle of Man. Zinc sulphide is white, but blende is often black in consequence of the presence of iron. Calamine, which contains carbonate of zinc, is less abundant with us than blende, but it is obtained in Spain, in the United States and elsewhere. *Willemite*, or zinc orthosilicate (Zn_2SiO_4), is interesting as affording us an example of an orthosilicate (see silicic acid, 308).

In order to extract zinc from the native sulphide or carbonate, the ore is roasted in a current of air to convert it into oxide, and the oxide is then reduced by heating it to bright redness with powdered coal in iron retorts *A* (Fig. 135). The zinc, which is volatile at the temperature employed, distils away and is condensed*. The zinc of

* Further details concerning this and similar processes must be sought in a treatise on metallurgy, such as those of Sir W. C. Roberts Austin, and Professors Huntington and McMillan.

commerce, which is known as *spelter*, usually contains iron, lead, tin, cadmium, copper and arsenic in varying proportions.

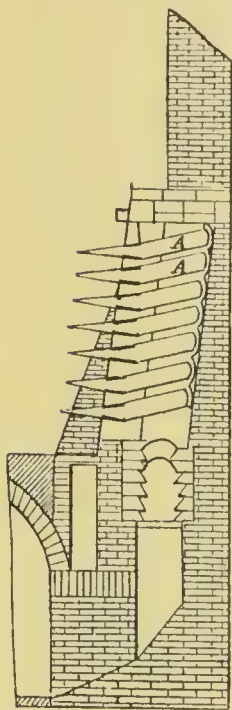


Fig. 135.

Pure zinc may be obtained by dissolving the crude metal in dilute acid; treating the solution with hydrogen sulphide to precipitate tin, cadmium, copper, lead and arsenic; reprecipitating the zinc as carbonate; igniting the carbonate to convert it into oxide; reducing the oxide by means of sugar charcoal, and finally redistilling the metal from a porcelain retort.

The physical properties of zinc vary with its temperature. It is a bluish-white metal which tarnishes in damp air. When cold it is brittle, but if it is heated to 120° – 150° it becomes malleable, and may be rolled, or hammered into sheets, and after this treatment it retains its malleability. On the other hand at 210° it may be powdered. It melts at a little above 400° and boils below 1000° . Its density in the solid state varies from 6.8 to 7.2. The density of its vapour is about 32.5 ($H = 1$), and therefore, since its atomic weight is 65, we conclude that its molecule consists of a single atom. [How would you find the vapour density of zinc?]

EXPERIMENT 276. To learn if zinc, like magnesium, burns in air. Heat some zinc strongly in a crucible, and expose it to the air. It will ignite, burning with a greenish flame, and giving off white flakes of zinc oxide.

Pure zinc dissolves but slowly in dilute sulphuric acid * [verify this], but, as we know, the crude metal is used for making hydrogen.

Amalgamate a sheet of zinc by rubbing it, first with dilute sulphuric acid and then with quicksilver. Immerse the amalgamated metal in dilute acid. You will find that it behaves like the pure metal. On the other hand, zinc coated with copper acts much more freely with acids and even with water (see 125, *c*). Zinc is also attacked by caustic alkalis, with which it gives zinc oxide, or hydroxide, and free hydrogen.

Zinc is largely used for making *galvanized iron*, which is made by

* It dissolves more freely if a little copper sulphate is added to the acid.

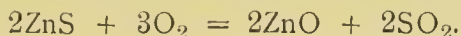
dipping sheets of clean iron in a bath of molten zinc. The coat of zinc which adheres to the surface of the iron greatly retards the process of rusting.

408. Alloys of zinc. *Brass* is composed of copper and zinc. Until 1780 it was made by heating copper in contact with calamine and carbon. At present the zinc is added to melted copper, care being taken to avoid oxidizing the zinc by holding it underneath the copper until it is melted.

Dutch metal and *Dutch gold leaf* are also composed of copper and zinc, and *Muntz metal* is a variety of brass containing three parts of copper to two of zinc. It is used for sheathing the bottoms of ships, and is more malleable when hot than ordinary brass.

409. Zinc chloride (ZnCl_2) is very soluble and fusible. It is very deliquescent, and is a very powerful dehydrating agent.

410. Zinc oxide (ZnO) is a basic oxide which may be made by igniting zinc carbonate or by roasting the sulphide :—



It is reduced when strongly heated with carbon. Zinc oxide is used, under the name of *zinc white*, for making paints which do not blacken when exposed to hydrogen sulphide. When hot it is yellow, but when cold it is nearly white.

Zinc oxide and hydroxide are insoluble in water, but soluble in acids and in fixed alkalis such as soda and potash.

411. Zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), or *white vitriol*, is difficult to distinguish from sulphate of magnesium. Like the latter salt it loses six molecular proportions of water at 100° , and forms double salts with sulphates of potassium and ammonium ($\text{ZnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$). Zinc sulphate is a by-product in the making of hydrogen, but it is obtained on the large scale by roasting blende, and treating the roasted mass with water.

412. Zinc carbonate (ZnCO_3) is a white insoluble solid, which is decomposed by heat. It occurs native, as *calamine*. When made by adding an alkaline carbonate to a solution of a salt of zinc it contains oxide.

413. Zinc sulphide (ZnS). This compound also occurs native, as *blende* (407); when pure, it is nearly white. It is insoluble in

water, but soluble in acids, and is one of the chief sources of the metal.

Dissolve some zinc sulphate in water, add to the solution some solution of ammonium sulphide. A *white* precipitate, $\text{ZnS} \cdot \text{H}_2\text{O}$, will fall.

Potash, soda, and ammonia throw down precipitates of zinc hydroxide from solutions containing soluble zinc salts. These precipitates are soluble in excess of the alkali in each case.

When a compound of zinc is strongly heated before the blow-pipe it leaves a residue of zinc oxide. When this is reheated with a drop of solution of nitrate of cobalt, it acquires a characteristic green colour.

CADMIUM (Cd): Atomic weight, 111.6.

414. Cadmium is extracted from the ores of zinc. It is more volatile than zinc, and therefore is chiefly found in those portions of the zinc which condense at the earlier stages of the process described in 407. To extract cadmium from zinc, the mixture may be dissolved in dilute hydrochloric acid, and treated with hydrogen sulphide. This throws down a yellow precipitate of cadmium sulphide, but leaves the zinc in solution. The sulphide of cadmium is washed, and roasted in air to convert it into oxide, which is reduced by heating it with carbon in a retort.

Cadmium resembles tin in appearance, and, like tin, it gives a cry when bent. It is malleable and ductile at ordinary temperatures, but brittle at 80° . It melts at 321° , and boils at about 770° . Its density is 8.6.

The density of its vapour, 56 ($H = 1$), shows us that its molecules are monatomic, like those of zinc. It burns in air if strongly heated, and dissolves in mineral acids, but less rapidly than magnesium or commercial zinc.

Cadmium is one of the constituents of the alloy called 'fusible metal,' which contains one part of cadmium, four of bismuth, two of lead, and one of tin, and which fuses at 61° .

Like the other metals of the magnesium group cadmium forms a basic oxide (CdO). And a peroxide is said to exist. Its sulphate has the composition $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, but if deposited from hot solutions it corresponds to the formula $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ and it forms double salts such as $\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. [Compare with magnesium sulphate.] This salt is more soluble in warm water than cold, but its solubility is said to diminish at temperatures above 68° .

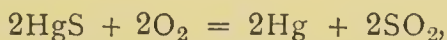
It may be recognized in combination by its yellow sulphide, which is insoluble in dilute hydrochloric acid and also in alkaline sulphides.

CHAPTER XXVII

MERCURY (Hg) : Atomic weight, 198.5

415. THIS remarkable metal, like zinc and cadmium, has monatomic molecules. It is also divalent.

Mercury is sometimes found free in nature, but it is usually met with as *cinnabar* (HgS). It is chiefly found at Almaden in Spain, at Idria in Austria, and in Mexico and California. Mercury is obtained by roasting cinnabar in air in a suitable furnace. Sulphur dioxide and mercury are formed :—



and are conducted into chambers and flues in which the quicksilver condenses, whilst the sulphur dioxide passes on and escapes. Sometimes the ore is reduced by roasting it with lime or scrap iron. It is usually imported in iron bottles holding about seventy-five pounds. Mercury, when nearly free from foreign metals, exhibits a clean bright surface, and leaves no 'tail' when globules are allowed to run over the surface of a table. Impure mercury may be purified, to some extent, by prolonged shaking with dilute nitric acid. It must afterwards be well washed with water and dried, but it is very difficult to obtain mercury free from other metals. Mercury is a nearly silver-white liquid metal; its freezing-point is -39° , and its boiling-point $+357^\circ$. When solid it is a soft metallic substance. The density of liquid mercury at 0° is 13.59. The density of its vapour is about 100.

The alloys of mercury are called *amalgams*. Many amalgams are known, as mercury readily dissolves several other metals. This property is made use of in extracting gold and silver from their ores. An amalgam of tin and mercury is used for making mirrors; and other amalgams are used by dentists. Mercury is useful for thermometers, and is employed by chemists in place of water for collecting gases which cannot be collected over the latter liquid.

Pure mercury is not sensibly attacked by the air at ordinary temperatures, but it is slowly oxidized at temperatures near its boiling-point (see 4). Cold hydrochloric acid and sulphuric acid act but slightly on quicksilver, whether they be strong or dilute; but strong hot sulphuric acid converts it into the sulphate, part of the acid being

reduced to sulphur dioxide (425). It is converted into nitrate of mercury by dilute and by strong nitric acid. It combines directly with chlorine and iodine (see Expt. 82, I-III).

We have already prepared mercury from its oxide on the small scale (340).

MERCUROUS AND MERCURIC SALTS.

416. EXPERIMENT 277. (a) Shake a considerable mass of quicksilver, say 50 grams, with a little very dilute nitric acid in a stoppered bottle vigorously for some time. Decant the solution and label it *A*. (b) Warm about a gram of quicksilver with a little strong nitric acid till a drop of the diluted solution no longer gives a precipitate on the addition of a drop of solution of hydrogen chloride. Dilute the product with water, and label it *B*.

Now add to portions of each of these solutions separately :—

1. A little solution of caustic soda. Solution *A* will give a black precipitate. Solution *B* will give a yellow precipitate.

Collect, dry and heat the two precipitates in test tubes. Both will yield oxygen and quicksilver.

2. Add to each of the solutions a little dilute hydrochloric acid. *A* will give a white curdy precipitate. *B* will give no precipitate, unless the solution is rather strong, but if you concentrate it cautiously, it will yield crystals on cooling.

Both the precipitate and the crystals will yield quicksilver if they be heated in a hard-glass tube with slaked lime, and both will give evidence that they contain chlorine if examined in the manner described in 146.

These various results suggest the idea that there may be two nitrates, two oxides, and two chlorides of mercury, and more exact experiments have shown that this is undoubtedly the case. The two oxides are termed mercurous oxide and mercuric oxide; the two nitrates are mercurous and mercuric nitrate, and similarly the chlorides are known as mercurous chloride and mercuric chloride. We have here a well-marked difference between mercury and the other members of Group II. The former yields two classes of salts, the others only one*.

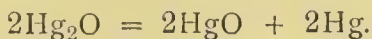
417. Mercurous oxide (Hg_2O) is a dark powder. It may be obtained by adding potash to a solution of mercurous nitrate, as

* This statement might be verified by making a similar set of experiments with zinc or magnesium.

described above, or by digesting calomel (Hg_2Cl_2) with solution of potash :—



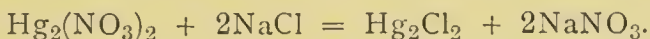
It changes, under the influence of light, into quicksilver and mercuric oxide :—



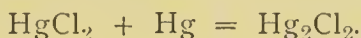
418. Mercuric oxide or red oxide of mercury (HgO).
EXPERIMENT 278. To make red oxide of mercury. Heat a little nitrate of mercury cautiously in a dish, in a fume closet. Red fumes will be evolved [what are these?], and a bright red residue of mercuric oxide will be left in the dish.

Mercuric oxide is resolved by heat into quicksilver and oxygen, but as the oxide made by igniting the nitrate is apt to contain traces of nitrate, the precipitated oxide is to be preferred as a source of oxygen. It is used in pharmacy under the name of 'red precipitate.'

419. Mercurous chloride or calomel (Hg_2Cl_2) is precipitated from solutions of mercurous nitrate by adding a soluble chloride :—



It is made on the large scale by triturating mercuric chloride with quicksilver and a little spirit of wine *, and subliming the mixture :—



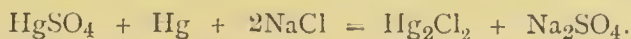
The product is ground to a powder, and well washed with water to remove every trace of mercuric chloride, as this latter compound is highly poisonous.

Calomel is a nearly white, dense solid. It is insoluble in water and in dilute nitric acid, but strong nitric acid oxidizes it. In strong daylight it is gradually transformed into mercuric chloride and mercury :—



Its vapour density is 119.0 ($\text{H} = 1$) †. Hence its formula might be supposed to be HgCl ; but the fact that the salt is readily resolved into mercuric chloride and mercury makes it probable that the vapour

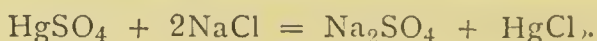
* A mixture of mercuric sulphate, mercury, and common salt may also be used :—



† Mr. Baker has lately observed that dry mercurous chloride has a normal vapour density.

in question consists of a mixture of mercuric chloride and mercury (see dissociation, 220).

420. Mercuric chloride or corrosive sublimate (HgCl_2). Mercuric chloride may be made by direct combination (Expt. 82, I); by dissolving mercuric oxide in hot hydrochloric acid, or by dissolving quicksilver in 'aqua regia.' On cooling the hot solutions they deposit the salt in small crystals. On the manufacturing scale, a mixture of salt and mercuric sulphate, in equivalent proportions, is sublimed:—



The sublimate forms a very dense crystalline solid which is not very soluble in water, but which dissolves better in alcohol. It is intensely poisonous, and is a very valuable antiseptic.

421. Mercurous iodide (Hg_2I_2). (Expt. 82, III).

422. Mercuric iodide (HgI_2). This salt has already been studied. It is a brilliant scarlet solid which readily forms soluble double salts (Expt. 82, III).

423. Nitrates of mercury. We have already learnt how the two nitrates of mercury may be prepared, and how they may be distinguished from each other (416).

Mercurous nitrate ($\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) forms crystals. *Mercuric nitrate* ($2\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$) is deposited as a crystalline solid by the spontaneous evaporation of its solution in the presence of free nitric acid. Both these salts are decomposed by water, less soluble basic compounds being formed.

424. Mercurous sulphate (Hg_2SO_4) is a slightly soluble crystalline salt, which may be obtained as a white precipitate by adding a solution of a soluble sulphate to solution of mercurous nitrate.

425. Mercuric sulphate (HgSO_4). Heat a little strong sulphuric acid with a globule of mercury in a dish, on a sand bath, in a fume closet. Sulphur dioxide will be given off, owing to the reduction of part of the acid, and mercuric sulphate will remain:—



Mercuric sulphate is insoluble in water, or rather it reacts with water producing an acid sulphate together with a yellow insoluble basic salt ($\text{HgSO}_4 \cdot 2\text{HgO}$), called *turpeth mineral*.

426. Mercuric sulphide (HgS). This is the chief constituent of cinnabar. It is extensively prepared for use as a pigment, *vermilion*, by subliming an intimate mixture of mercury and sulphur. The Chinese are especially skilful in preparing this substance. Mercuric sulphide can be prepared in the wet way by the action of hydrogen sulphide on solutions of mercuric salts. When the gas is first passed into the solution a white precipitate is apt to form. This consists of sulphide of mercury combined with a part of the original salt. A further supply of hydrogen sulphide converts all the mercury salt into the sulphide, which then forms a black solid; this yields vermilion when it is sublimed.

Mercury forms a number of very interesting compounds by replacing the hydrogen of ammonia:—

Thus we can obtain a mercurioso-diammonium chloride ($\text{N}_2\text{H}_6\text{Hg}_2\text{Cl}_2$) by the action of ammonia gas (NH_3) on dry calomel (Hg_2Cl_2), and a dimercurioso-ammonium chloride ($\text{NH}_2\text{Hg}_2\text{Cl}$) by adding solution of ammonia to calomel. If a solution of mercuric chloride (HgCl_2) is added to a hot solution of ammonium chloride containing some ammonia, as long as the precipitate redissolves, we obtain crystals of mercurio-diammonium chloride ($\text{N}_2\text{H}_6\text{Hg}''\text{Cl}_2$). Nessler's solution is believed to form an analogous compound, and a nitride N_2Hg_3 and other compounds are known.

Compounds containing mercury may be recognized by their volatility, and by the fact that they deposit quicksilver on sheets of copper when the latter is warmed in solutions containing them. *Mercuric salts* may be distinguished by the yellow oxide which they form when treated with potash or soda, and by the scarlet iodide which is precipitated when their solutions are mixed with potassium iodide. Mercurous salts yield a dark precipitate (Hg_2O) with caustic alkali, a greenish-yellow one (Hg_2I_2) with potassium iodide, and give white precipitates (Hg_2Cl_2) with soluble chlorides.

CHAPTER XXVIII

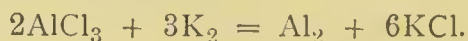
THE METALS OF THE ALUMINIUM GROUP

427. ALUMINIUM, gallium, indium, and thallium belong to the third, fifth, seventh, and eleventh series of Group III. These metals form chlorides of the type MCl_3 and oxides corresponding to the

formula M_2O_3 , which are not very basic; they may be regarded as trivalent; and they form alums (see 201). Thallium differs considerably from the other three elements.

ALUMINIUM (Al): Atomic weight, 26.9.

428. Aluminium is abundant in *felspar* and in *clay*. The metal was discovered in 1828 by Wöhler, who prepared it by reducing aluminium chloride with potassium:—



It is now made by passing electricity between rods of carbon in a box, or furnace, lined with carbon, and containing alumina (Al_2O_3) dissolved in molten cryolite. The temperature of the furnace and its contents is maintained by the electric discharge, and fresh supplies of alumina are added from time to time. In another form of the process alumina is employed without the addition of cryolite. In both modifications of the process carbon monoxide is one of the products of the change.

Aluminium is remarkable for its lightness (density about 2.6), and is about as hard as zinc. It is nearly as white as silver, and takes a high polish. It is not tarnished by exposure to air. When in very thin sheets, it may be burnt without much difficulty, and it can be used to reduce the oxides of chromium and manganese.

The most useful alloys containing aluminium are those in which it is associated with copper. The so-called aluminium gold is an alloy containing 90-95 per cent. of copper. Within this range of composition the alloys may have very considerable tensile strength. Aluminium melts at 625° .

EXPERIMENT 279. Some chemical properties of aluminium.

1. Place some fragments of aluminium in dilute hydrochloric acid or sulphuric acid. They will be attacked very slowly.

2. Place some aluminium in a fairly concentrated solution of potash or soda. The metal will dissolve, replacing hydrogen which will be liberated.

3. Dissolve a crystal of nitre in some solution of potash or soda, and add fragments of aluminium. Soon the odour of ammonia will become evident owing to the reduction of the nitre by nascent hydrogen. Methods of measuring the nitrates in drinking water have been based on this reaction.

429. Alumina (Al_2O_3). Alumina occurs in nature as *corundum*, *ruby*, *sapphire*, and *emery*.

EXPERIMENT 280. Some uses and properties of alumina.

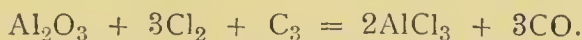
1. *To make alumina.* Add slight excess of ammonia to a solution of common alum, collect the gelatinous precipitate of hydrated alumina ($\text{Al}(\text{HO})_3$, or $\text{Al}_2(\text{HO})_6$), dry it, and heat the residue strongly to expel water.

2. Add a little freshly precipitated alumina to solutions of caustic soda and of dilute sulphuric acid respectively. It will dissolve in both, but you will find it impossible to neutralize the acid with alumina owing to its feeble basic qualities, and many of its salts are distinctly acid to litmus.

3. *The use of alumina as a mordant in dyeing.* Mix a few drops of solution of alizarin with some solution of alum. Then add a few drops of solution of ammonia. The precipitated alumina will carry down the alizarin in the form of a *lake*. The attraction of certain bases for organic matter, which causes the formation of 'lakes,' has long been made useful in the dyeing of cotton goods. The 'lakes' are generated within the fibres of the cotton, from which they are not easily removed when the goods are afterwards washed.

When alumina is dissolved in soda or potash, compounds called *aluminates* are formed, and potassium aluminate ($\text{K}_2\text{Al}_2\text{O}_4$) is said to have been isolated by concentrating such a solution.

430. Aluminium chloride (AlCl_3 , or Al_2Cl_6). Aluminium chloride was formerly the chief source of metallic aluminium. It is usually prepared by passing chlorine over an intimate mixture of alumina and carbon heated strongly in a clay retort:—



It may also be obtained by heating the metal in chlorine.

Aluminium chloride is a white deliquescent solid. At high temperatures its vapour density suggests the formula AlCl_3 , but below 400° its density agrees with the formula Al_2Cl_6 . If a solution of aluminium chloride be evaporated, it yields crystals of a hydrated chloride ($\text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$); if these be heated they are converted into water, hydrochloric acid, and alumina. Consequently, the anhydrous chloride of aluminium cannot be prepared by evaporating an aqueous solution of the salt. Like many other chlorides it readily forms double salts.

One of these, viz. $\text{NaCl}, \text{AlCl}_3$, has been used as a source of the metal.

Aluminium also forms a fluoride (AlF_3), and cryolite, which is a beautiful white stone found in Greenland, is a double fluoride of aluminium and sodium ($3\text{NaF}, \text{AlF}_3$).

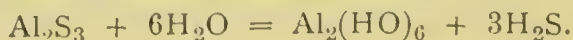
431. Aluminium sulphate and alum. When hydrated alumina is dissolved in dilute sulphuric acid, a soluble white salt with a sweetish astringent taste is formed. If a proper proportion of sulphate of potassium or sulphate of ammonium be added to this solution, an alum will be formed.

EXPERIMENT 281. To obtain alum from clay. Heat 20 grams of white china clay with 15 c.c. of oil of vitriol to near the fuming-point for some hours. When the action is complete, boil the product with six or seven times its weight of water, filter off the residue of silica, evaporate the solution to a syrup, and allow it to cool. It will yield crystals of aluminic sulphate ($\text{Al}_2(\text{SO}_4)_3, 16\text{H}_2\text{O}$). If the proper proportion of sulphate of potassium, or of sulphate of ammonium, be added to some of the aluminic sulphate in solution, alum ($\text{Al}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4, 24\text{H}_2\text{O}$, or $\text{Al}_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4, 24\text{H}_2\text{O}$) will be formed. (For the other alums see 201, also 38).

432. Aluminium silicates. Many of these compounds occur in nature. Thus china clay, or kaolin, is a silicate of aluminium produced by the decomposition of felspar ($\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$). The less pure varieties of clay, many of which contain iron, owe their origin to similar substances; shale and slate also contain alumina and silica.

The application of clay to the making of pottery has already been considered (see 310).

Aluminium may be recognized in its compounds by the colourless gelatinous precipitates of hydrated alumina which they yield when soda, potash, or ammonia are added to their solutions; and by the solubility of these precipitates in acids, and in excess of potash or soda. When alumina is moistened with nitrate of cobalt, and strongly heated in the blow-pipe flame, it assumes a fine blue colour. Hydrogen sulphide does not precipitate aluminium from solutions of its salts. But ammonium sulphide throws down a precipitate of hydrated alumina ($\text{Al}_2(\text{HO})_6$). We may attribute this to the fact that sulphide of alumina is decomposed by water:—



GALLIUM (Ga) : Atomic weight, 69.5.

433. When the table on p. 181 was drawn up, its authors were unable to place any known element in series 5, Group III. Therefore the discovery of gallium in 1875 by Lecoq de Boisbaudran was received with great interest. Gallium was first recognized, by means of the spectroscope, in a blende from the Pyrenees. It is obtained in the free state by electrolyzing a solution of its oxide in potash or ammonia. It is a hard, white metal, which takes a good polish. Its density is 5.9, its melting-point is about 30° , but when melted it may remain fluid till it falls to 2° . Its dichloride is soluble and deliquescent. Gallium is not readily oxidized. It dissolves in dilute mineral acids. It forms an ammonia alum which crystallizes in octahedra. Its sulphide, which is soluble in dilute hydrochloric acid, is white, and might easily be mistaken for zinc sulphide.

INDIUM (In) : Atomic weight, 113.1.

434. Indium was also discovered by means of the spectroscope. It was first found in a zinc-blende from Freiberg. Its density, 7.4, is higher than that of gallium, and its melting-point, 176° , is intermediate between those of gallium and thallium.

Like the other metals of this group it is a white metal which is soluble in acids. Its hydroxide is soluble in acids and also in potash and soda. Its sulphide is yellow. It exhibits characteristic spectral lines in the violet and blue (see 336).

THALLIUM (Tl) : Atomic weight, 202.6.

435. This metal was discovered by Crookes in 1861 in deposits from the flues of a sulphuric acid manufactory. By means of the spectroscope he observed a remarkable green line in the spectrum of a residue obtained by distilling impure selenium extracted from this deposit, and thus he was led to discover the new element.

EXPERIMENT 282. Properties of thallium. If the student can obtain a decigram or two of metallic thallium he may verify the following statements, or some of the chief of them :—

1. Notice that the metal is preserved under a liquid, viz. glycerine. This is done to preserve it from the air. If a fragment be cleaned and exposed to the air it will be found to tarnish quickly.

2. Find its melting-point (19), using a small bath of melted paraffin. It melts at 294° .

3. Rub a fragment of clean metallic thallium on white paper. Notice that the metal leaves a streak somewhat resembling that made by lead. Watch this at intervals. You will find that it gradually fades. [How do you explain this?]

4. Warm a minute fragment of thallium with a drop of hydrochloric acid, and hold the solution in a Bunsen flame on a clean platinum wire. Observe the characteristic green colouration given to the flame. If you have a spectroscope observe the spectrum given by the green flame.

5. Make a streak with thallium on some neutral litmus paper, and expose it to damp air. Notice that the streak presently becomes blue. This is due to the production of thallos hydroxide (TlHO , or $\text{Tl}_2\text{H}_2\text{O}_2$), which is a soluble, strongly alkaline substance.

Thallium also forms a thallic oxide (Tl_2O_3); this is the chief product of burning the metal in oxygen; it loses oxygen at a red heat.

6. Warm the fragment of thallium used for 2 with a drop of strong sulphuric acid. Hydrogen will be given off*, and if the product be diluted you will obtain a dilute solution of thallos sulphate (Tl_2SO_4) from which an alum may be prepared. A thallic sulphate ($\text{Tl}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$) corresponding to thallic oxide is also known.

7. Add a drop of a solution of common salt to the solution of thallos sulphate. A white, curdy precipitate of thallos chloride (TlCl) will fall; this dissolves on warming like lead chloride. Other chlorides, as the trichloride (TlCl_3), are known.

Thallos carbonate (Tl_2CO_3) is formed when the metal is exposed to damp carbon dioxide. It is a soluble, alkaline, and crystalline substance.

From these results you will see that whilst thallium resembles lead in some of its properties, and whilst thallos chloride might be mistaken for lead chloride, thallos oxide, hydroxide, and carbonate have many of the characters of the corresponding compounds of the alkali metals, and thallos sulphate forms an alum with aluminium sulphate.

Thallium and its compounds are very poisonous.

Information concerning the elements scandium, yttrium, and lanthanum, which also occur in Group III, must be sought in one of the larger manuals.

* Sodium also gives off hydrogen when treated with strong sulphuric acid.

CHAPTER XXIX

TIN, LEAD, AND GERMANIUM

436. The chief metals of Group IV are tin and lead, but titanium, germanium, zirconium, cerium, and thorium also belong to this group.

TIN (Sn) : Atomic weight, 118.1.

437. Tin mines have been worked from very early times, when the metal was extensively used for making bronze. Among the important sources of supply are Cornwall, where the tin mines were formerly of greater importance than at present, the island of Banca, Saxony, Australia, and Bohemia. Tin is usually associated with oxygen, arsenic, sulphur, copper, iron, and tungsten.

Tin is chiefly found as oxide of tin in *tinestone* or *cassiterite*, sometimes as sulphide (SnS_2). The ore is broken up, sorted, washed, and roasted in air* to expel arsenic and sulphur, and then reduced by heating it with anthracite coal and a little lime, or some fluor-spar, in a reverberatory furnace. The crude tin is usually refined by two processes known respectively as *liquation* and *poling*.

Liquation consists in heating ingots of crude tin upon the hearth of a furnace. The tin fuses and runs away, leaving behind it such infusible particles as it may have contained.

The process of *poling* consists in plunging stakes of green wood under the surface of molten tin. This causes a brisk evolution of steam, which exposes a large surface of the metal to the air, and promotes the rapid oxidizing of impurities, which are afterwards removed in the form of dross.

Refined tin is so brittle, when heated nearly to its melting-point, that it can be broken into small fragments by letting blocks of it fall from a height; tin thus granulated is known as *grain tin*. If a piece of tin be held near the ear and bent, a peculiar grating sound, known as the *cry of tin*, may be perceived. Tin is the most easily fusible of all the common metals. Its melting-point is 232° . Its density is 7.3. It is but little corroded by exposure to the air or by dilute

* If tungsten is present the ore is treated with 'salt-cake' in a furnace to remove the tungsten, as tungstate of soda.

acid fumes, and therefore it is used extensively to protect the surfaces of more oxidizable metals such as iron; but it is freely oxidized when it is heated above its melting-point in air.

Tin-plate consists of sheet iron coated with tin. To make it, sheets of iron are cleaned by immersing them in warm dilute sulphuric acid to dissolve or loosen any adherent oxide, and then scoured with sand and water. They are then rubbed between rollers of very hard material to polish them, annealed, again treated with acid, scoured and dipped into tin melted under tallow or palm oil. Finally, they are run between two rollers immersed in melted fat to protect the metal from exposure to air, which squeeze all excess of tin from the surface of the plates.

Tinning copper. Copper vessels, especially if they be not kept perfectly clean, are apt to introduce copper into food prepared in them, therefore they are usually tinned internally as a precaution against poisoning. This is done by rubbing the inner surface of the vessel whilst hot with sal-ammoniac to remove every trace of oxide, sprinkling the clean hot metal with resin, which melts and protects it from oxidation, and then rubbing melted tin over the copper.

438. Bronze. This is the name given to alloys of copper and tin. The composition of these alloys varies considerably. Thus for coinage 95 per cent. of copper, 4 per cent. of tin, and 1 per cent. of zinc may be used. Alloys containing from 8.5 per cent. to 10 per cent. of tin have been extensively employed under the name of gun-metal, and the ancients used axes, &c., made of such an alloy, and hardened by heating them to redness, and then cooling them slowly. Bell-metal contains 20 or 22 per cent., and speculum metal about 33 per cent. of tin.

Other alloys containing tin are solder and pewter, which contain tin and lead. An amalgam of tin and mercury is used for making mirrors.

Tin is soluble in strong hydrochloric acid, but it is converted by nitric acid into a white insoluble solid.

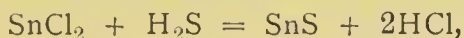
439. The two chlorides of tin. EXPERIMENT 283. Digest 5 grams of granulated tin with 15 c.c. of strong hydrochloric acid and a few small scraps of platinum in a flask, on a sand bath. Divide the solution obtained into two parts; dilute one part, and warm the other with half its volume of strong nitric acid until no more red fumes are evolved, and dilute the product with water.

1. Pass hydrogen sulphide through small portions of both solutions.

The first will give a dark brown precipitate, which consists of stannous sulphide (SnS). The second will give a yellow precipitate of stannic sulphide (SnS_2).

2. Warm both solutions with solution of mercuric chloride. The first will give a white precipitate of calomel, which becomes black if excess of the tin salt be employed. The second will give no such precipitate.

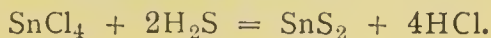
Explanation of the above results. When tin is dissolved in hydrochloric acid, stannous chloride (SnCl_2) is formed. This gives stannous sulphide (SnS), which is brown, with hydrogen sulphide:—



and reduces mercuric chloride to mercurous chloride, and then to mercury, owing to the readiness with which it combines with chlorine. Thus:—



On the other hand, the stannous chloride is converted into stannic chloride (SnCl_4) when warmed with aqua regia. This latter salt, being saturated, has no reducing power, but it yields yellow stannic sulphide when it is treated with hydrogen sulphide:—



Stannous chloride (SnCl_2) is a volatile solid (B.P. about 600°). It is deposited in fine hydrated crystals ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) from a concentrated solution of tin in hydrochloric acid. It is used as a mordant (see 429, 3) by calico printers, and is, as we have seen, a powerful reducing agent.

Stannic chloride (SnCl_4) may be made in the anhydrous state by passing dried chlorine over tin. It is a colourless, fuming liquid, which boils at 114° . It forms hydrated crystals corresponding to the formula $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$. This salt and also its double salts are useful to the dyer.

440. Monoxide of tin or stannous oxide (SnO). This is a black solid which when heated in air readily forms the dioxide (SnO_2). Its hydrate is a white solid which may be obtained by adding an alkaline carbonate to a solution of stannous chloride. The hydrated oxide is soluble in potash and is used by dyers.

441. Stannic oxide (SnO_2) occurs native in *tinestone*. It may be obtained by heating metallic tin or stannous oxide in air as a white

or nearly white powder, which is used for polishing glass, steel, &c., and is very insoluble. The hydrated oxide occurs as stannic acid (H_2SnO_3) and metastannic acid ($\text{H}_{10}\text{Sn}_5\text{O}_{15}$).

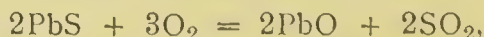
442. Stannic acid. If stannic oxide is fused with sodium hydroxide it produces sodium stannate (Na_2SnO_3), which will dissolve in water and is used as a mordant by dyers. If an acid be cautiously added to a solution of this compound a gelatinous precipitate of stannic acid will be formed. This substance reddens litmus, and resembles the acids more closely than the bases, although it is soluble in strong acids. If it be strongly heated it is converted into stannic oxide (SnO_2).

443. Metastannic acid. Pour some strong nitric acid on some granulated tin in a capacious flask, warming them cautiously, if necessary. A vigorous action will set in, dense red fumes will be given off, and a white solid will be formed. This is metastannic acid. When dried it has the composition $\text{H}_{10}\text{Sn}_5\text{O}_{15}$, but only two-tenths of its hydrogen is replaceable by metals. It is insoluble in acids; but dissolves slowly in *cold* solutions of the alkaline hydroxides, forming metastannates.

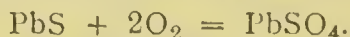
LEAD (Pb) : Atomic weight, 205.35.

444. Only two lead ores are sufficiently abundant to serve as sources of lead on the large scale, viz. *galena* (PbS); and *cerussite* or *white lead ore* (PbCO_3). Galena, which is by far the more abundant, is found in Derbyshire, Cumberland, Flintshire, in some parts of Scotland, and in the Isle of Man. It is also plentiful in Spain, Saxony, Bohemia, France, and in the United States. Most galena contains silver, and when the proportion is large enough to be extracted with profit, the galena is said to be *argentiferous*. *Cerussite* is much less common, and is chiefly found associated with galena in parts of Germany, Spain, and the United States.

In smelting lead ore the galena is roasted; some of the sulphur escapes as sulphur dioxide and lead oxide is formed:—

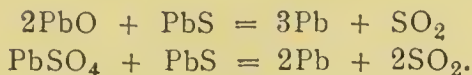


at the same time another portion of the ore is oxidized to sulphate:—



The mixture of oxide and sulphate with the remaining sulphide is

then heated to a higher temperature and produces lead and sulphur dioxide :—



If the ore contains silica, lime is added to prevent loss of lead in the form of silicate.

The furnaces employed vary in different localities. In some parts of England a reverberatory furnace is used (Fig. 136), in other places the work is carried out in small blast furnaces (see Fig. 138).

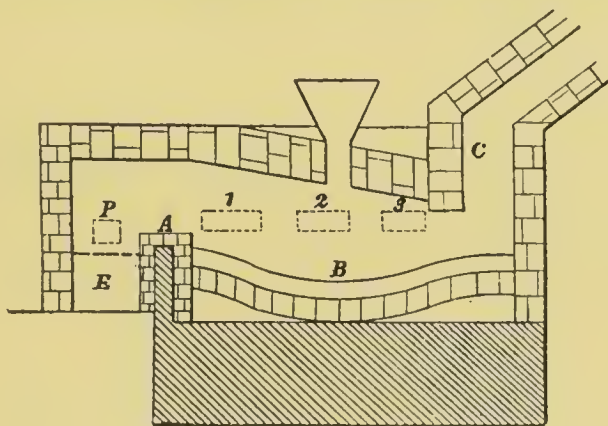


Fig. 136.

B, the hearth; *A*, fire-bridge; *C*, flue or chimney; *P*, fire-door for introducing fuel; *E*, the ash-pit; 1, 2, 3, doors to give access to the hearth and its contents. There are also tap-holes for the lead and slag which are not shown. The lining of the hearth, *B*, is made by spreading semi-fused slag from previous operations, with sand, over the brickwork to a depth of 6 inches or more. The form of the hearth enables the lead to run to its bottom, which is so hollowed out that the metal flows to a sort of well at one side of the furnace, where a tap-hole is provided. As the lead runs from the furnace it is collected in pots, where it is stirred and skimmed. It is afterwards run into moulds.

The crude lead may contain antimony, copper and iron, which make it hard. These may be partially removed by calcining the lead in a furnace. The impurities rise to the surface, and are removed quickly to prevent them from being gradually reabsorbed by the molten lead. At the earlier stages of this process the foreign metals separate in the metallic state, but towards the end of the process as oxides.

Lead is easily prepared on the small scale by reducing one of its oxides with powdered carbon (see Expt. 260), or by the action of fused potassium cyanide, as in the case of tin (see Expt. 259).

For desilverizing lead see 545.

Lead is valuable in the arts on account of the readiness with which it can be rolled into sheets, or be made to take any desired shape by hammering. On the other hand, the poisonous nature of its compounds limits its usefulness by making it unsuitable for many domestic purposes. Its want of tenacity makes it impossible to draw thin wires of lead. It melts at 330° , and is slightly volatile at a red heat. Its density is 11.4 (water = 1).

445. The alloys of lead are of considerable importance. Type-metal is an alloy of lead and antimony, or of lead, copper, and antimony. Bullets are often made of lead hardened by tin. Small shot are made from lead hardened by adding a very small proportion of arsenic.

Pewter consists of four parts of tin with one of lead. An alloy having this composition has a low melting-point and may be used safely for drinking vessels, but if the proportion of lead be higher the pewter may be corroded by hard (sour) beer. The best solder is composed of two parts of tin to one of lead.

The formulæ of most of the compounds mentioned below might suggest that lead is divalent, but the existence of a tetraethide ($\text{Pb}(\text{C}_2\text{H}_5)_4$), of a perchloride (PbCl_4), and of a peracetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$)*, shows us that lead, like tin, is quadrivalent.

Lead is attacked by dilute nitric acid, but it is dissolved slowly by other dilute acids; it is dissolved slightly by water containing air and carbon dioxide and by solutions containing nitrates, but water which contains sulphates, phosphates, or carbonates has very little action.

446. Lead dichloride (PbCl_2) is a white salt. It is precipitated when soluble chlorides are added to solutions of lead nitrate or acetate. It is sparingly soluble in cold water, but more soluble in hot water.

Bromide of lead (PbBr_2) is also a colourless insoluble solid, but lead iodide (PbI_2) is a beautiful, fusible, yellow salt which crystallizes from hot water in fine golden spangles. When strongly heated in air it gives off iodine, leaving a residue of lead oxyiodide.

447. Lead perchloride (PbCl_4). A solution of this salt is formed when chlorine is passed through a solution of lead chloride in hydrochloric acid. The anhydrous salt is a yellow liquid which solidifies at -15° . Water gradually converts it into lead peroxide and hydrochloric acid. It forms double salts with alkaline chlorides which are more stable.

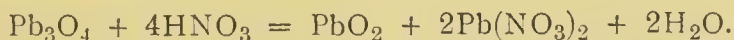
* Hutchinson and Pollard,

448. Plumbous oxide (Pb_2O). When oxalate of lead is heated to 300° out of contact with air, it leaves a grey residue which absorbs oxygen with avidity. This is the suboxide.

449. Plumbic oxide (PbO) is known as *litharge* or *massicot*. It is made by calcining the metal in air, or by heating the carbonate to a low red heat. Plumbic oxide is a dense, straw-coloured solid. It is a basic oxide*, and, though almost insoluble, gives an alkaline reaction with litmus. It dissolves in melted potash, and in the molten state it attacks silica and its compounds vigorously. It is one of the components of flint glass. A hydrated oxide of lead falls as a precipitate when ammonia is added to an aqueous solution of a salt of lead; this is colourless, like the oxide it is slightly soluble, and when moist absorbs carbon dioxide.

450. Triplumbic tetroxide (Pb_3O_4). This substance is commonly known as *minium* or *red lead*. It is made by heating litharge with a little antimony in a current of air. It is used as a pigment, also by glass-makers, and is one of the constituents of the red lead used by plumbers and others. When strongly heated it gives off oxygen (see also 451).

451. Lead peroxide, puce oxide of lead. EXPERIMENT 284. To make peroxide of lead. Warm a few grams of red lead with some dilute nitric acid. The red lead will soon be replaced by a brown powder. Collect this powder on a filter; it consists of lead peroxide (PbO_2). The change by which it is formed may be represented as follows :—



If you concentrate the filtrate and allow it to cool, it will deposit crystals of lead nitrate. Lead dioxide may also be made by warming a solution of lead acetate with excess of bleaching powder.

Lead peroxide gives up half its oxygen when it is strongly heated. When warmed with hydrochloric acid it yields a chloride and free chlorine, like other peroxides*. By warming it with concentrated acetic acid it may be made to yield a tetra-acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$), which crystallizes on cooling. On the other hand it acts as a weak acid to strong bases yielding plumbates, e. g. $\text{K}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$. It is a powerful oxidizing agent, becoming ignited when rubbed in a mortar with sulphur.

* See 120.

Lead also forms a sesquioxide (Pb_2O_3). This is an orange-red powder which acts as a basic peroxide.

452. Lead monosulphide (PbS). In the form of galena this compound constitutes our chief source of lead. It occurs in fine crystals, which exhibit metallic lustre and resemble lead in appearance. It is obtained as a black precipitate by passing hydrogen sulphide through a solution of a salt of lead.

Owing to the blackness of lead sulphide, strips of bibulous paper soaked with a solution of lead nitrate, or acetate, are often made use of for detecting small quantities of hydrogen sulphide.

453. Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) is a soluble crystalline salt, which may be prepared easily by dissolving litharge or metallic lead in nitric acid, and evaporating the solution till crystals form. When heated it yields nitric peroxide (see 237).

454. Lead sulphate (PbSO_4). This is a very dense insoluble salt; it falls as a white powder when a solution containing a salt of lead is mixed with dilute sulphuric acid, or with a solution of a soluble sulphate. It is nearly insoluble in strong acids, but dissolves in solutions of ammonium salts and in caustic alkalis. It can be obtained by the direct oxidation of galena.

455. Lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$). This salt, like lead nitrate, is soluble in water. It has a sweetish astringent taste, and is known as *sugar of lead*. It is very poisonous.

456. Lead and silica. Lead silicate is one of the components of flint glass, and it forms the glaze of many varieties of earthenware (see 310 and 311).

457. Lead carbonate (PbCO_3) occurs native, as *cerussite*.

White lead is a basic carbonate of lead of variable composition, which is used in great quantities in pigments. The most interesting process for making white lead is the 'Dutch process.' Lead cast in the form of gratings, or in thin sheets, is exposed simultaneously to the vapour of acetic acid and to carbon dioxide, the latter being generated by fermenting tan or stable manure. It is supposed that the acetic acid and air form layers of basic acetate of lead on the metal, and that the carbon dioxide gradually converts this into a basic carbonate, liberating the acetic acid, which attacks fresh portions of the metal until the whole, or nearly the whole, is converted into white lead. The crust

of white lead is afterwards separated from any remaining lead, and ground to a powder. In one form of the process lead in rolls, *b* and *c* (Fig. 137), is placed on ledges in earthen pots. The latter contain a little acetic acid at *a*. A number of these pots are packed between layers of tan in tiers in a chamber, and there left until the process is complete.

The process occupies a considerable time, and several quicker methods have been devised, but the product of the Dutch process is usually considered to be superior to those which are made by the rival methods.

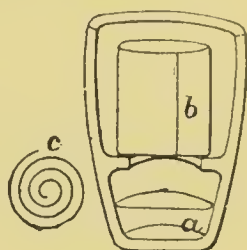


Fig. 137.

Most of the compounds of lead are poisonous. The sulphate, owing perhaps to its insolubility, is less so than many of the others. Consequently a solution of a soluble sulphate, such as Epsom salts, forms a useful antidote in cases of lead poisoning. Painters, and those who work in white lead works, &c., are apt to suffer from chronic lead poisoning, which is accompanied by violent colic and nervous prostration, and may end in death if it be neglected.

GERMANIUM (Ge) : Atomic weight, 71.9.

458. Germanium was discovered (1886) in a sulphide of silver and germanium. The metal has been obtained by reducing its oxide with carbon. It is brittle, crystalline, and melts at 900° . It forms two oxides, a tetrafluoride, a tetrachloride, a tetrabromide, a tetraiodide, and a tetraethide ($\text{Ge}(\text{C}_2\text{H}_5)_4$). Its sulphide (GeS_2) is white, and is soluble in solutions of alkaline hydrosulphides. Its fluoride forms a compound corresponding to silicofluoric acid, viz. H_2GeF_6 (175).

Germanium corresponds in atomic weight and properties with the hypothetical *ekasilicon* of Mendelejeff.

Titanium, zirconium, cerium, and thorium are also quadrivalent. They form volatile tetrachlorides and tetrafluorides, which are apt to enter into the formation of compounds analogous to the silicofluorides, e.g. H_2TiF_6 . Several of them are distinguished from silicon by forming oxysalts, such as sulphates. It will be noticed that these four elements belong to series 4, 6, 8, and 12, in Group IV, whilst germanium, tin, and lead belong to series 5, 7, and 11.

CHAPTER XXX

THE METAL-LIKE ELEMENTS OF GROUP V. ANTIMONY AND BISMUTH

WE have already learnt that antimony and bismuth, with nitrogen, phosphorus, arsenic, and some less common elements, constitute Group V. These elements, like those of Group IV, illustrate the fact that some of the members of a group may be metallic and others non-metallic in character, and that when both metals and non-metals occur in a given group, the metallic qualities are exhibited by those members which have the higher atomic weights; as may be seen by comparing the properties of carbon and silicon with those of tin and lead, or the properties of nitrogen and phosphorus with those of bismuth.

ANTIMONY (Sb) : Atomic weight, 119.8.

459. Antimony is chiefly extracted from *antimony glance* or *grey antimony* (Sb_2S_3), which is found in several parts of Europe, Japan, Australia, and in the United States. It is frequently associated with iron pyrites, quartz, and heavy-spar. The sulphide is separated from these by heating the crude ore on a reverberatory furnace provided with a concave hearth lined with carbon. The antimony sulphide melts, and is drawn off into moulds; it still contains arsenic, iron, and lead, as well as antimony and sulphur.

In England, sulphide of antimony is reduced by heating it in crucibles with metallic iron, which withdraws the sulphur from the antimony:—



Antimony melts at 425° . Its density is 6.7. If a fragment of the metal be closely examined, it will be seen to possess a crystalline structure. It is so brittle that a sharp tap with a hammer will break it into fragments which exhibit irregular surfaces composed of shining plates. Antimony is chiefly used for making certain valuable alloys. Thus *type-metal* contains 25 per cent. of antimony, with 75 per cent. of lead, and *stereo-metal* is composed of tin, lead, and antimony.

EXPERIMENT 285. The chemical properties of antimony. Throw a little powdered antimony into a jar of chlorine. The metal will burn, forming antimony chloride.

Heat some antimony before the blow-pipe on a block of charcoal. Notice that it easily fuses, and that the globules of molten metal emit white fumes. These consist of oxide of antimony.

460. Antimony hydride, stibine (SbH_3). EXPERIMENT 286. Set up a small apparatus for generating hydrogen; when all the air is expelled ignite the gas at a jet, and add a few drops of a solution of antimony chloride to the contents of the apparatus. The flame will become livid owing to the presence of antimony hydride in the hydrogen.

A deposit of antimony may be obtained by holding a cold porcelain dish against the flame, or by passing the gas through a hot tube (compare arsenic, 268). The deposit is insoluble in bleaching solution. If antimony hydride is passed through a solution of silver nitrate, a black precipitate is formed. This has been regarded as silver antimonide (Ag_3Sb), but according to a recent observer silver and antimonious acid are formed.

Antimony hydride may be made in larger quantities by dissolving an alloy of zinc and antimony in dilute hydrochloric acid.

461. Oxides of antimony. Three of these are known:—

Antimonous oxide (Sb_4O_6). This oxide occurs in two forms which are isomorphous with the forms of arsenious oxide (As_4O_6).

The fumes emitted by burning antimony consist of this oxide, and it is formed when an alkaline carbonate is added to solution of antimony trichloride (SbCl_3).

Antimonous oxide is soluble in hydrochloric acid and, when warmed with sodium and hydrogen tartrate, forms a solution from which crystals of *tartar emetic* ($\text{K}(\text{SbO})'\text{C}_4\text{H}_4\text{O}_6, \text{H}_2\text{O}$) can be obtained. It also dissolves in alkalis, but the antimonites are very instable.

462. Antimony tetroxide (Sb_2O_4) is formed when antimonous oxide is roasted in air. It is a white powder, which dissolves in hydrochloric acid, and which is partly soluble in tartar emetic, leaving a residue of the pentoxide (Sb_2O_5).

463. Antimony pentoxide (Sb_2O_5). This may be obtained by heating antimonic acid strongly, but not to a red heat. If very strongly heated, it is reduced to the tetroxide.

EXPERIMENT 287. **Antimonic acid.** Warm some powdered antimony with strong nitric acid. Red nitrous fumes will be evolved, and the metal will be converted into a white solid. This when dried

over sulphuric acid is metantimonic acid (HSbO_3). Three hydrates of antimony pentoxide have been met with, viz. *orthoantimonic acid* (H_3SbO_4), which when heated to 100° yields *pyroantimonic acid* ($\text{H}_4\text{Sb}_2\text{O}_7$), and is converted into *metantimonic acid* (HSbO_3) at 200° . The acid potassium salt of pyroantimonic acid ($\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$) is remarkable for giving precipitates with solutions containing salts of sodium, for which it may be used as a test.

464. Antimony trichloride (SbCl_3). This compound may be obtained in solution by treating antimonious sulphide with strong hydrochloric acid. It is also formed by the action of chlorine on antimony. Antimony trichloride is a very deliquescent, crystalline solid, which was formerly called 'butter of antimony.' It melts at about 73° , boils at 223° , and is soluble in strong hydrochloric acid. If water is added to a solution of antimony trichloride, a white precipitate containing *stibyl monochloride* or oxychloride of antimony (SbOCl) is thrown down.

465. Antimony pentachloride (SbCl_5). This may be made most simply by passing chlorine into the trichloride. It is a fuming volatile liquid, which freezes at -6° . It is resolved into free chlorine, and the trichloride when boiled under atmospheric pressure (compare PCl_5); but if it be vaporized at a low pressure, its vapour density corresponds to the formula SbCl_5 . It may be used as a chlorinating agent. If mixed with hot water, it yields pyroantimonic acid and hydrochloric acid.

Antimony forms a bromide (SbBr_3), and a tri-iodide (SbI_3); also a trifluoride (SbF_3) and a pentafluoride (SbF_5). The last two compounds are made by dissolving the corresponding oxides in hydrofluoric acid. They form double salts with fluorides of the alkali metals. The first is crystalline and deliquescent, the second has not been crystallized.

466. Antimony sulphides. *Antimony trisulphide* (Sb_2S_3). This occurs native, as *antimony glance*.

EXPERIMENT 288. To prepare antimony trisulphide. Dilute some solution of antimony trichloride with water till it forms a slight permanent precipitate, add just enough hydrochloric acid to redissolve this, and pass hydrogen sulphide through the solution. A fine orange-red coloured precipitate of the hydrated sulphide of antimony will fall. If this be heated much above 200° it will give off water and become black.

Warm some of the precipitated sulphide with solution of ammonium sulphide. It will dissolve (compare 271)*. It is also soluble in solutions containing caustic soda or potash.

A pentasulphide of antimony (Sb_2S_5) may be obtained by the action of hydrogen sulphide on a solution of the pentachloride in water containing tartaric acid. Like the trisulphide, it dissolves in solutions of alkaline sulphides forming thioantimonates†.

467. Tartar emetic ($\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$). Warm some antimonous oxide with about an equal weight of cream of tartar dissolved in water. When the oxide is nearly all dissolved, filter and concentrate the solution, and leave it to crystallize. It will deposit crystals of a compound in which the radicle antimonyl (SbO) replaces the hydrogen of cream of tartar.

The compounds of antimony are poisonous.

BISMUTH (Bi): Atomic weight, 206.9.

468. Bismuth, which is not very plentiful, usually occurs associated with other metals. Most of our supplies of it are received from Australia and Bolivia. It is often found native, and is then separated from its ores by heating them in a liquation furnace (see 437), so that the bismuth, which melts at 266° , may run from the other materials. It is obtained from the sulphide, or *bismuth glance*, and from the carbonate, by roasting them and reducing the oxide with iron and carbon, a slag being added to act as a flux. It is then liquated (437).

Bismuth is a highly crystalline greyish-white metal, which melts at 266° . It is not ductile nor malleable; it boils at a white heat. Its density is 9.8, and is reduced by strong pressure.

It is a component of fusible metal (see 414), and of some kinds of type-metal, to which it gives the habit of expanding during cooling in a valuable degree.

Hydrochloric acid and sulphuric acid attack bismuth slowly; it readily dissolves in nitric acid, forming a nitrate ($\text{Bi}(\text{NO}_3)_3$). At high temperatures it burns in air. It also combines directly with chlorine.

469. Trioxide of bismuth (Bi_2O_3) is precipitated as a hydrate ($\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or BiHO_2), when potassium hydroxide or ammonia is

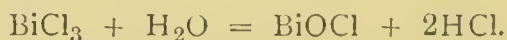
* These reactions may be used as a means of recognizing antimony.

† e. g. K_3SbS_4 .

added to a solution of the nitrate; when this is heated, it yields the oxide which is soluble in nitric and hydrochloric acids, but *not* in alkalis. (Compare the oxides of arsenic.)

470. Bismuth pentoxide (Bi_2O_5) is produced by passing chlorine through solution of potash in which the trioxide is suspended, and warming the product with nitric acid to remove any trioxide that may remain. It is a red powder which, like antimony pentoxide, yields a tetroxide (Bi_2O_4) when heated. Bismuth pentoxide is a peroxide and possesses some acidic power, but the bismuthates have not been fully investigated.

471. Bismuth trichloride (BiCl_3). If bismuth is heated in a current of chlorine this compound is obtained as a sublimate. It is fusible, volatile and colourless. It may also be made by dissolving bismuth in aqua regia. Bismuth trichloride reacts with water forming a basic chloride BiOCl :—



The precipitation does not approach completion, however, unless the proportion of water be very large in proportion to that of the bismuth chloride.

472. Bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$). If a solution of bismuth in nitric acid is concentrated it yields crystals corresponding to the above formula. Bismuth nitrate is deliquescent and soluble in dilute nitric acid, but if it be added to water a basic nitrate ($\text{BiONO}_3 \cdot \text{H}_2\text{O}$) is formed. The latter compound is used in medicine.

473. Bismuth sulphide (Bi_2S_3) is a black solid; it is formed when hydrogen sulphide acts on solutions containing bismuth, and it also occurs in nature. It is insoluble in dilute solutions of hydrochloric acid, and it is not soluble in alkaline sulphides like the sulphides of antimony and arsenic.

Bismuth may be recognized by its sulphide, and by the readiness with which it forms the above-mentioned basic chloride and nitrate.

The student should carefully compare the properties of antimony and bismuth, and of their chief compounds, with those of nitrogen, phosphorus, and arsenic. He should particularly notice the transition from non-metal to metal as he proceeds from elements of low atomic weight to those which have higher atomic weight.

474. The other members of Group V are vanadium, niobium, and

tantalum. The first of these is a light grey crystalline substance which exhibits metallic lustre. It is not volatile. It combines readily with nitrogen, but does not tarnish in air, and it burns in oxygen and chlorine. Sir Henry Roscoe, who first prepared pure vanadium, has shown that vanadium is a quinivalent element from studies of its oxides and oxychlorides, and from the fact that the vanadates are isomorphous with the phosphates.

CHAPTER XXXI

THE METALS OF GROUP VI

475. Chromium, molybdenum, tungsten, and uranium.

We have already studied four members of this group, viz. oxygen, sulphur, selenium, and tellurium; these, with the exception of oxygen, belong to odd series. The remaining four elements belong to even series; they are remarkable for the variety of the colours exhibited by their compounds, for their tendency to produce acidic oxides of the type RO_3 , and for the tendency of the salts of chromic, molybdic, tungstic, and uranic acids to combine with the trioxides (see potassium bichromate, 484). Molybdenum, tungsten, and uranium form both tetrachlorides and pentachlorides.

These elements appear to be sexvalent.

CHROMIUM (Cr) : Atomic weight, 51.7.

476. The chief source of chromium is *chrome ironstone* (FeOCr_2O_3). It is also found in an earthy deposit known as *chrome ochre* and as lead chromate. The colour of the emerald, of green serpentine, and of some other rocks is due to the presence of chromium.

Metallic chromium has recently been prepared by Moissan in comparatively large quantities by reducing chromic oxide with carbon in the electric furnace. It may also be made easily by reducing chromic oxide (Cr_2O_3) with powdered aluminium as described in Experiment 297, p. 465.

It is a brilliant white, not very heavy metal, density 6.92, which is harder than glass. It is not magnetic. At a dull red heat it forms chromous chloride in an atmosphere of hydrogen chloride, and it is dissolved by hot, strong sulphuric acid with an evolution of sulphur

dioxide; it is attacked also by hot dilute sulphuric acid. It is oxidized by the air much less readily than iron, and is attacked but slowly by nitric acid or aqua regia.

477. Chromous chloride (CrCl_2). This may be made by heating chromic chloride to low redness, in a current of hydrogen gas. It is a white crystalline salt, which gives a fine blue solution. Owing to the readiness with which this solution absorbs oxygen it is sometimes employed as a reagent in gas analysis.

478. Chromic chloride (Cr_2Cl_6 or CrCl_3) is an exceedingly beautiful pale-violet coloured salt which does not dissolve in water unless a small quantity of the dichloride is present, in which case it yields a green solution. A solution of the green salt may also be obtained by dissolving chromic hydroxide in hydrochloric acid. By evaporating this solution *in vacuo* we obtain a green crystalline mass containing the hydrated salt, but if the latter be strongly heated hydrogen chloride is evolved, and basic chlorides remain (compare aluminium chloride, 430). Anhydrous chromic chloride is made by exposing chromic oxide to the action of chlorine in the presence of carbon at a red heat, or by heating the hydrated chloride in the presence of gaseous hydrochloric acid.

479. Chromium monoxide (CrO). This is precipitated in a hydrated form by adding potash to a solution of the dichloride of chromium; like the latter it absorbs oxygen greedily. It yields blue salts with acids, which are readily oxidized.

480. Chromic oxide, chromium sesquioxide (Cr_2O_3). This substance is used as a pigment in painting on porcelain, and in the manufacture of coloured glass and enamels.

EXPERIMENT 289. **The preparation and properties of chromic oxide.** Heat a little chromate of mercury strongly in a covered crucible in a fume closet, or in the open air. The quicksilver and part of the oxygen will be expelled, and a green residue of chromic oxide will remain.

1. Fuse a little chromic oxide in a bead of fused borax, on the end of a platinum wire, and observe the effect.

2. Fuse a little of the oxide with some nitre. The change observed is due to the forming of a chromate.

Dissolve a few grams of chromium sulphate, or some chrome alum, in water, and add an equivalent quantity of soda or potash. A green and more or less gelatinous precipitate of chromic hydroxide will be

thrown down. Collect and dry this precipitate, and compare its properties with those of the anhydrous oxide.

3. Repeat the above experiment, but add a considerable excess of potash. You will obtain a fine green solution (compare alumina, 429). Warm a little of the green solution with some hydrogen dioxide or with sodium peroxide. Notice that it becomes yellow owing to the formation of chromate (K_2CrO_4).

481. Chromic sulphate ($\text{Cr}_2(\text{SO}_4)_3$). This salt is said to be red when dry, but its solutions are green or violet in colour. It is formed by dissolving chromic oxide in sulphuric acid.

482. Chrome alum ($(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$). If you add one molecular proportion of sulphate of ammonium, or sulphate of potassium, to a warm solution containing one molecular proportion of chromic sulphate, and set the solution aside, it will gradually deposit beautiful purple crystals of chrome alum. If the purple crystals are heated with water they reproduce the green form, but the solution will in time again yield the violet crystalline variety.

EXPERIMENT 290. **To prepare chrome alum from potassium bichromate.** Add a small excess of sulphuric acid to a solution of potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in warm water. Then add gradually sulphurous acid, oxalic acid, or sulphuretted hydrogen in slight excess, filter the solution, if necessary, and leave it to evaporate. Crystals of chrome alum will form after some delay. [Work out the equation for the change which occurs.]

483. Chromium trioxide or chromic anhydride (CrO_3). This may be regarded as the anhydride of chromic acid (H_2CrO_4), just as sulphur trioxide is the anhydride of sulphuric acid.

EXPERIMENT 291. **The preparation and properties of chromic anhydride.** Add three volumes of oil of vitriol to two volumes of a cold saturated solution of potassium bichromate, and allow the mixture to cool and crystallize. Drain the liquid from the crystals on a funnel, press the crystals between two porous tiles, and preserve them in a well-stoppered bottle.

1. Add a few of the red crystals to a few drops of water. Notice that they form a yellow solution, which expels carbon dioxide from alkaline carbonates.

2. Allow the solution obtained in 1 to evaporate. It will deposit pale yellow crystals of a chromate.

3. Pour a little absolute alcohol on a few crystals of chromic anhy-

dride, and apply heat. The red colour of the anhydride will quickly change to green, owing to its reduction, and the alcohol will probably ignite.

4. Heat some chromic anhydride with oil of vitriol. Notice whether oxygen is evolved, and whether a green solution of chromic sulphate is formed when the product is dissolved in water.

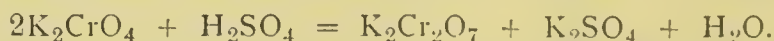
5. Warm some chromic anhydride with hydrochloric acid. Observe whether chlorine is evolved, and whether the anhydride is reduced.

6. Heat some chromic anhydride strongly. Notice that it gives off oxygen, leaving a residue of chromic oxide (Cr_2O_3).

From these various experiments we learn that chromic anhydride is an acidic oxide, and also a powerful oxidizer. It is therefore an acid peroxide (see 120).

484. The chromates. The salts of chromic acid are of considerable importance, several of them being useful in the arts. The normal chromates are frequently isomorphous (338) with the sulphates.

The most interesting compound derived from chromic acid is the so-called potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). To make this salt * fuse some chrome ironstone or chromic oxide with nitre in a large porcelain crucible, extract the product with water, and acidify the solution of chromate of potassium with sulphuric acid to produce bichromate :—



The potassium bichromate may then be crystallized from water in orange-red crystals, which melt at about 400° , and yield oxygen when strongly heated.

Potassium chromate is a pale yellow salt prepared from the bichromate by adding potash, and the insoluble chromates, such as those of mercury and lead, may be made from soluble chromates by precipitation; thus lead chromate or chrome yellow (PbCrO_4) is formed by adding a solution of a lead salt to a soluble chromate; the chromates of silver and mercury are insoluble and red.

Potassium bichromate is extensively used as an oxidizing agent. It is not, as will be seen, an acid salt analogous to the bisulphate (KHSO_4), but an anhydrochromate ($\text{K}_2\text{CrO}_4, \text{CrO}_3$) analogous to the anhydrosulphates or pyrosulphates derived from pyrosulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$) (193).

EXPERIMENT 292. **To make chromyl chloride (CrO_2Cl_2).** Warm

* On the large scale chrome ironstone is roasted with potassium carbonate and lime in air.

equal weights of potassium bichromate ($K_2Cr_2O_7$) and common salt ($NaCl$), well mixed, with oil of vitriol in a very small retort provided with a well cooled condenser, and placed in a fume chamber. Dense red vapours of chromyl chloride will be given off, and will condense to a dark-red liquid not unlike bromine in appearance, which boils at 116° .

Pass some of the vapour into water. It will dissolve, giving a yellow solution. Neutralize some of this solution and add nitrate of silver gradually. It will yield, first a white precipitate of silver chloride, afterwards a chocolate-red precipitate of silver chromate (Ag_2CrO_4). Its action with water may therefore be represented as follows :—



485. Perchromic acid. EXPERIMENT 293. Dissolve a little potassium bichromate in water, add a few drops of sulphuric acid, some ether, then some solution of hydrogen dioxide (H_2O_2), and shake them together. The ether will assume a beautiful deep-blue tint. The blue ethereal solution is supposed to contain perchromic acid ($H_2Cr_2O_8$ or $HCrO_4$) (compare persulphates, 204), or a compound of this substance with hydrogen peroxide. It is very unstable, and soon decomposes.

The student should now compare those chromium compounds which are most rich in oxygen, viz. chromium trioxide, the chromates, the bichromates, and perchromic acid with the corresponding compounds of sulphur. He will then understand why this element is assigned a place in Group VI (p. 181).

For a fuller account of the compounds of chromium and for an account of the other members of Group VI the student must consult one of the larger works on chemistry.

CHAPTER XXXII

IRON. MANGANESE. COBALT. NICKEL

IRON is so much more important than the other members of this group that it will be convenient to study this metal before manganese.

IRON (Fe) : Atomic weight, 55.5.

486. Iron occurs in the metallic state in some of the basaltic rocks, and in meteorites, and it is occasionally met with in isolated masses, which are supposed to be of meteoric origin. Native iron is not plentiful and usually contains nickel, and sometimes other metals, sulphur, phosphorus, &c. On the other hand, oxide and sulphide of iron are found very widely spread in nature, and compounds of iron are present in many rocks, in plants, and in the blood of animals. Iron also occurs as carbonate, chloride, or sulphate in many natural waters.

487. Sources of iron. The ores from which iron is chiefly manufactured contain oxides or carbonates. The following are among the most important :—

Magnetic ore. *Magnetite* *. This consists chiefly of the magnetic oxide (Fe_3O_4) ; it is met with also in the form of *smithy scales*, and is formed by the action of steam on iron heated to redness (see Expt. 52). It occurs abundantly in the north of Europe and in North America, in masses of an iron-black or grey colour. The pure ore contains 72 per cent. of iron.

Hæmatites. *Red hæmatite*, so called from its colour, is sometimes found in dense hard masses which have the appearance of being made up of bundles of fibres, but it also occurs in soft earthy masses. Hæmatite is more common than magnetite, and is found in various localities in Great Britain. It consists of ferric oxide (Fe_2O_3), and yields excellent iron. If pure it contains about 70 per cent. of iron.

Brown hæmatite. This also contains ferric oxide, but in this case the oxide is associated with from 10 to 14 per cent. of water, hence the proportion of iron is smaller than in red hæmatite. It is found in Great Britain, but occurs more extensively in France and Spain.

Specular iron ore, like the hæmatites, consists of ferric oxide ; it occurs in crystalline masses, or separate crystals which exhibit considerable lustre. It is found in the island of Elba, and large deposits occur in Russia and Spain, and in various parts of America.

Spathic iron ore consists of ferrous carbonate. This ore usually contains some manganese. It owes its name to its appearance, 'Spath' meaning spar in German. It has been found in some parts of England, and contains about 48 per cent. of iron.

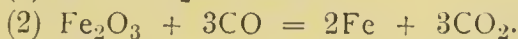
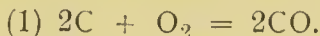
* One variety of this is the loadstone, which was used for magnetizing steel.

Argillaceous iron ore. Clay ironstone. Clay-band. These ores contain carbonate of iron intimately mixed with clay. They are abundant in various parts of Great Britain, and are extensively smelted. They frequently occur in layers which alternate with beds of coal and limestone, and the fact that the same, or closely adjacent, mines yield the ore, and also the coal and the limestone required for smelting it, has been a great advantage to the iron-smelters of this country, and of Belgium and Silesia, where the same conditions also occur. The proportion of iron varies from 17 to 45 per cent.

Black-band ore. This may be described as a clay-band ironstone containing a considerable amount of bituminous matter.

Iron pyrites (FeS_2) is plentiful. It is very extensively burnt by the makers of oil of vitriol, and the oxide left after the sulphur has been removed is sometimes smelted for the sake of its iron.

488. Extracting iron from its ores. The early iron-smelters obtained iron by heating rich iron ores with charcoal in the presence of air. Carbonic oxide was formed, and this reduced the oxide of iron:—



At the same time the earthy matter present, usually silica, combined with some ferrous oxide produced by reduction of the peroxide, and formed a fusible 'slag,' and thus the primitive workers obtained a semi-fluid or pasty mass of iron, more or less mingled with slag which could be removed by squeezing and hammering the mass whilst still hot. The furnaces employed were sometimes small towers of clay open at the top, and provided with small apertures below to admit the necessary supply of air; sometimes they consisted of holes dug near the edge of a bank, with an opening let into the side of the bank which pierced the furnace at its bottom and admitted tubes of clay to act as tuyères (489). Such a furnace is charged* by introducing lighted wood, and throwing layers of charcoal and ore alternately upon the burning material. From time to time the slag is allowed to run off, and in about twenty-four hours as much as 90 lb. of iron may be made in a small furnace.

489. The blast furnace. The following figure (Fig. 138) will give a general idea of the blast furnaces at present used for reducing

* This method is still practised in Burmah. See *Metals*, by Huntington and McMillan.

iron ores on the large scale. The body of the furnace, which is from 20 to 30 metres high, is constructed of firebrick, and cased with iron plates, the whole being braced together with hoops of iron and supported by iron columns (*CC*) on a bed of concrete. The ore, mixed with coal and limestone, is introduced at *A*, after lowering the cone. As the mixture descends, the ore becomes heated, and is exposed to the

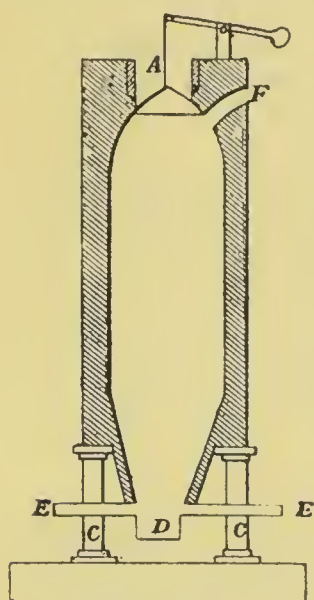


Fig. 138.

action of combustible gases, which probably soon reduce it to the metallic state. As it falls into the hotter parts of the furnace, the reduced iron melts, slag is formed by the action of the limestone on the silica in the ore, and both gradually descend to the well, or hearth, of the furnace at *D*, where the iron sinks to the bottom, owing to its high density, whilst the slag floats above. As the well fills, the upper layer of slag reaches certain openings provided for the purpose and runs away. The molten iron is also run off at suitable intervals. It is received in moulds of sand, and when it has solidified constitutes *pig-iron*.

The chemical changes by which the iron is produced consist, broadly speaking, in the forming of carbon monoxide at the lower parts of the furnace, where the carbon meets oxygen in heated air forced in through the tubes *EE* (tuyères); and in the reduction of the oxide of iron by this carbon monoxide, and by gases produced by the destructive distillation of the coal, in the upper parts of the furnace.

But probably the iron thus produced would not melt and flow to the 'hearth' were it not that other changes also occur. In the first place some of the carbon monoxide appears to be resolved, at the temperature of the furnace, into carbon and carbon dioxide :—



and part of this carbon combines with the iron forming a carbide, or a mixture of carbides, which is more fusible than pure metallic iron.

And secondly, during the progress of the other changes the lime of the limestone combines with the silica, alumina, and magnesia present

in the ore forming a fusible substance known as *blast furnace slag*, which melts and falls with the fused metal into the well*.

The gases which reach the top of the furnace usually contain a good deal of combustible matter. They were formerly allowed to burn, but now are carried off by the pipe *F*, and made use of either for heating boilers to generate steam, which can be utilized for driving machinery, or to heat the air before it is introduced into the furnace by the tuyères.

A well constructed blast furnace, when once started, and if in good working order, may turn out from 1000 to 1500 tons of iron in a week, and in America they have furnaces which give a much larger output. When once a furnace is 'blown in' it may remain in action continuously night and day for months or years, until repairs become necessary.

490. Pig-iron. The iron collected from a blast furnace is always more or less carburized. It also contains most of the phosphorus and part of the sulphur which were present in the ore and fuel, together with some silica. Some ores contain manganese, and these yield iron containing this metal. When the proportion of manganese reaches 5 to 20 per cent. the product is termed *spiegeleisen*; if more manganese is present it is *ferro-manganese*, both of which are useful to the makers of steel.

The carbon in pig-iron appears to exist in two forms. When a sample of what is called 'grey cast iron' is dissolved in dilute acid, carbon is left in the form of graphite; but if 'white cast iron' be similarly treated, it leaves little graphite, owing to the fact that its carbon is in combination with the iron, and separates in the form of liquid or gaseous compounds. In grey cast iron the proportion of combined carbon is smaller than in white cast iron, hence the former contains relatively more metallic iron. Grey cast iron is softer and more easily filed or turned on a lathe than white cast iron, which can hardly be filed, and may be broken by a blow from a hammer which would only indent grey cast iron. Grey cast iron requires a higher temperature to melt it than white cast iron; but it becomes more thoroughly fluid, and so can more easily run into moulds. The two varieties of iron are readily distinguished by the fact that white cast iron throws off sparks or scintillates, as it runs from the

* This slag was formerly wasted; but bricks, cement, and even plates and dishes can be made from it; it is also sometimes used for road metal.

furnace, more freely than grey iron. Finally, grey iron is rather less dense than white, rusts more easily, and is more rapidly attacked by acids.

Pig-iron containing phosphorus becomes more fluid when melted, and therefore is very suitable for taking fine castings. The presence of this element reduces the strength of the iron, but this may be compensated for by the greater soundness of the castings.

491. Wrought iron or malleable iron, and steel. The composition of cast or pig iron varies considerably. The proportion of iron may rise as high as 97 per cent., or it may fall as low as 93 per cent., and considerable variations may occur in the proportions of its other components. It is hard, brittle and crystalline, and is therefore unsuited for many of the purposes to which we put iron. Pure iron, or the nearly pure iron next described, can be obtained with a fibrous texture; it is malleable and ductile, and can easily be welded at a red heat. It is known as *wrought iron* or *malleable iron*.

The process by which pig-iron is converted into wrought iron is usually called *puddling*, but sometimes the pig-iron is *refined* before it is puddled. The refining process consists in blowing air over the surface of melted pig-iron, by which means much of the silicon and a little carbon are oxidized and removed.

A puddling furnace is a kind of reverberatory furnace consisting of a fire-place *A* (Fig. 139), a hearth *B*, and a flue *E* leading to a chimney. The hearth is separated from the fire-place and the flue by two low walls known as the fire-bridge *C* and the flue-bridge *D*; these may be hollow and kept cool by the circulation of streams of water.

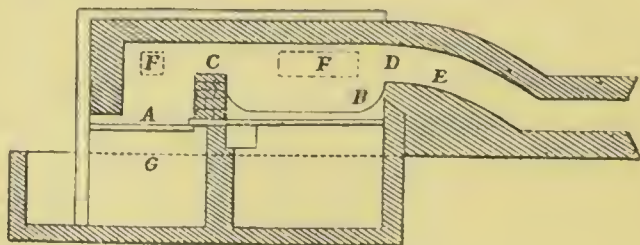


Fig. 139.

The hearth is formed of plates of iron supported by bars. The former are covered with a coating of substances rich in oxide of iron to a depth of about two inches. Working doors are provided at suitable positions as at *F* and *F'*, and *G* is the fire-pit.

The process of puddling is conducted as follows. The charge of iron is placed in *B*, and heated by flames from the fire, which is urged by a blast of air, if necessary, until the iron melts. Oxide of iron from slag in the lining of the hearth, which melts and gradually mingles with the molten metal, affords a supply of oxygen which oxidizes the silicon and some carbon. When the charge has been at a high temperature for a few minutes the heat applied is reduced, by shutting a damper, and the molten metal and oxide are well mixed by stirring. Presently a violent action sets in, the metal appears to boil, owing to the escape of carbon monoxide which burns in jets of blue flame, the metal gradually becomes less fluid, and ultimately, when only about 1 per cent. of carbon remains, it forms a pasty mass. It is then again heated more strongly, repeatedly broken up, and worked, at a reduced temperature, into masses of about 80 lb. weight. These are placed under a powerful hammer, which squeezes out the oxide and converts the metal into 'blooms.' Finally, these blooms are reheated and drawn out between grooved rollers into long bars, which are afterwards cut into pieces, bound together, and again hammered when hot, and drawn into single bars.

As the result of these various processes most of the carbon, silicon, sulphur, and phosphorus is oxidized and removed from the iron, and the metal becomes fibrous in texture, highly malleable and ductile, and, as mentioned before, capable of being welded when red-hot.

492. Steel is intermediate in composition between pig-iron and malleable iron. That is to say, it usually contains less carbon than the former, but more than the latter. One of the oldest methods of steel-making is the process of *cementation*. In this, bars of malleable iron of good quality are embedded in powdered charcoal mixed with some nitrogenous matter and a little alkali, in a firebrick box, which is heated to redness for some time. During this treatment the iron takes up some carbon, becoming harder and more fusible, but loses its malleability to some extent. The product of the operation is usually found to be blistered on its surface, and is known as *blister steel*; it is afterwards rendered more uniform by welding together several bars, and drawing them out while still hot; or it is broken up, melted, and cast into ingots to make *cast steel*.

Another method of making steel which is now employed on a very large scale is the **Bessemer process**. In this process melted pig-iron is introduced into a *converter*, previously heated (Fig. 140), and air is forced through it until the carbon and silicon are consumed. The

requisite amount of carbon, together with some manganese, is then introduced in the form of spiegeleisen or ferro-manganese (490), and afterwards the converter is inverted and the steel poured into moulds.

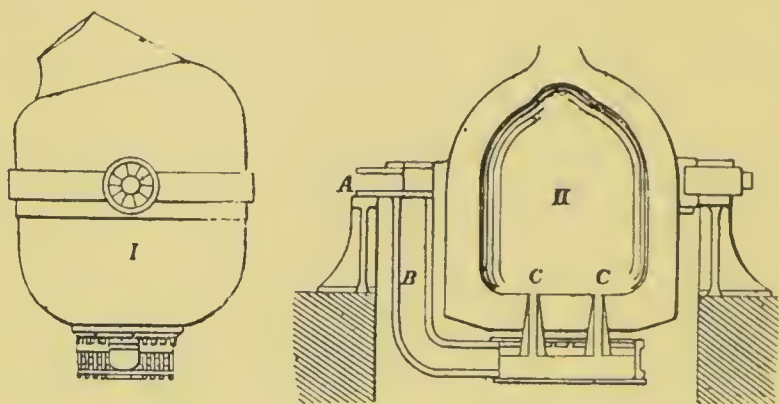


Fig. 140.

I. External view of Bessemer converter. II. Internal view. The air is introduced at the trunnion *A*, which is hollow, and passes by *B* to the jets *CC*.

The original Bessemer converters were lined with a siliceous fire-clay, and it was soon found that though the carbon and silicon were oxidized and removed from iron by their use, the phosphorus, which usually is present, could not thus be got rid of. This difficulty led to the introduction of the so-called *basic process* of Thomas and Gilchrist. In the basic process the converter is lined with calcined dolomite, that is, with a mixture of magnesia and lime, and some lime is introduced with the pig-iron. The base fixes the oxide of phosphorus as it is formed, so that it becomes possible to make a good steel from pig-iron containing phosphorus in considerable quantities.

Another method of making steel, called the *open-hearth process*, consists in decarburizing pig-iron by adding oxide of iron to the molten metal in a reverberatory furnace, and then introducing a proper proportion of spiegeleisen or ferro-manganese.

One great advantage of the modern methods of making steel consists in the fact that it is possible to regulate the proportion of carbon with great exactness, and thus to produce the quality of steel required for any given purpose.

The value of steel largely depends on the readiness with which its qualities may be made to suit the various needs of the worker in metals. If it be heated to between 700° and 800° , and then suddenly cooled,

by plunging it into water or mercury, it may be made hard enough to cut the hardest glass. If it be reheated and allowed to cool gradually it again becomes soft. It can therefore be fashioned when soft and malleable, and be hardened subsequently if that be desired. The degree of hardness attainable depends on the proportion of carbon in the steel, and it can be controlled by 'tempering.' To temper steel the previously hardened material is carefully reheated to a suitable temperature, which may be judged by the colour of the film of oxide which forms upon it, and then allowed to cool spontaneously or quenched in water.

493. The classification of steel and iron. In the previous pages, iron from various sources has been classified as pig-iron, steel, and malleable iron. And it has been stated that whilst pig-iron contains the greatest proportion of carbon, and steel a lesser proportion, malleable iron consists of almost pure metallic iron; and that steel is distinguished from the other forms of iron by the fact that it can be hardened and tempered. In practice, however, it has been found inconvenient of late years to limit the application of the term 'steel' in this way, and it has become customary to apply it to all metal produced by the Bessemer process, or by certain other processes, so that we now speak of steel rails, steel ships, &c., although the metal they are made of does not possess in any marked degree the properties of steel in the more limited sense of that word.

494. Properties of iron. Iron is a comparatively soft metal, highly tenacious and malleable; it possesses, when polished and free from rust, a silvery lustre, and exhibits, if broken, a crystalline fracture. Its density varies; for example, it is 7.88 (water=1) after fusion, whilst the density of iron deposited by electrolysis is about 8.14. It is said to expand when cooled below -40° ; and it need hardly be added that iron is highly magnetic.

Iron, as we have already seen, combines directly with chlorine, bromine, iodine, and sulphur. It is permanent in dry air at ordinary temperatures, but if it be plunged into a jar of oxygen when very hot, or when in contact with burning sulphur, it ignites, and heaps of scrap iron, in the form of tin-plate, have been known to catch fire and burn in air.

The rusting of iron, which consists in the formation of ferric oxide (Fe_2O_3), is understood to depend on the combined action of moisture and carbon dioxide. It is supposed that ferric carbonate forms,

and subsequently breaks up into iron rust and carbon dioxide, and that the latter substance at once attacks fresh portions of the adjacent iron. Although iron readily replaces the hydrogen of dilute mineral acids, it has but little action on water, except at high temperatures (see 52), or when it is finely divided.

Iron dissolves in nitric acid; when dilute acid is used ferrous nitrate ($\text{Fe}(\text{NO}_3)_2$) and ammonium nitrate are formed and remain in solution, but if the acid be very dilute some hydrogen may be evolved; if strong acid is used, a ferric salt is formed and nitric oxide is given off.

The passive state of iron. This remarkable phenomenon may be observed by plunging a clean iron rod into some warm concentrated nitric acid. When this is done no signs of action will be seen. It has been supposed that this curious phenomenon may be due to the forming of a film of an oxide of nitrogen, or possibly of magnetic oxide of iron, on the surface of the metal. The temperature at which it occurs depends on the strength of the acid employed, and is also influenced by the purity of the acid.

Finely divided iron combines with carbonic oxide, forming a compound having the composition $\text{Fe}(\text{CO})_5$. It is a viscous crystallizable liquid, which boils at about 103° .

495. Oxides of iron. Two oxides of iron have already been mentioned, viz. ferric oxide (Fe_2O_3) and magnetic oxide (Fe_3O_4), which occurs as magnetite, and is formed when iron and steam react at high temperatures. A third oxide, ferrous oxide (FeO), also exists, but it is very unfamiliar on account of the rapidity with which it is converted into ferric oxide by atmospheric oxygen.

496. Ferric oxide or sesquioxide of iron (Fe_2O_3). This oxide, as we have already learnt, occurs plentifully in nature both in the anhydrous state and in combination with water, as in brown hæmatite. It is isomorphous (338) with alumina, and is largely used as a source of iron. It may be prepared by adding excess of solution of ammonia to a solution of a ferric salt, washing the gelatinous precipitate of iron hydroxide with water, and heating it strongly.

Ferric oxide is also made by calcining ferrous sulphate (193). When made in this way it is known as 'rouge,' and is used as a pigment and for polishing glass and other substances. It is readily reduced when heated in a current of hydrogen or carbon monoxide

(Expt. 257), but it is not easily altered by the action of heat alone.

Ferric hydroxide can be obtained in solution by dialysis.

EXPERIMENT 294. Add recently precipitated moist ferric hydroxide to a fairly strong solution of ferric chloride gradually, and mix them well by shaking; when the hydroxide ceases to dissolve, filter the solution and place it in the dialyzer (309); renew the water in the outer vessel daily. In about ten days most of the iron chloride will have passed from the dialyzer, leaving a solution of the hydroxide behind. The solution thus obtained is used in medicine under the name of 'dialyzed iron'; it readily deposits ferric hydroxide on standing if traces of free acid or alkali are present.

497. Magnetic oxide of iron (Fe_3O_4). This may be regarded as a combination of ferrous and ferric oxides ($\text{FeO}, \text{Fe}_2\text{O}_3$), hence it is sometimes called *ferroso-ferric oxide*. It is a black solid, and an important source of iron.

Magnetic oxide of iron is formed by the action of steam on iron at a red heat (52); and it is found in meteorites and as a mineral in Northern Europe. It is not much acted upon by damp air or acid fumes, and attempts have been made to render iron pipes, &c., indifferent to exposure by submitting them when hot to the action of steam, but the process has not come into general use.

498. The ferrates. Although no acidic trioxide containing iron (compare chromic anhydride, 483) has yet been isolated, we are acquainted with salts in which iron forms a part of the acid radicle. These salts are termed *ferrates*. If considerable excess of a strong solution of potash be added to a solution of a ferric salt, and if chlorine be passed through the mixture, a dark powder will be deposited. This consists of potassium ferrate (K_2FeO_4); it is soluble in water, but somewhat unstable, and even when cold it slowly decomposes into oxygen, ferric oxide, and free alkali. The corresponding acid (H_2FeO_4) has not been met with, but an insoluble barium salt (BaFeO_4) has been made.

THE SALTS OF IRON.

499. Two classes of iron salts are known. These correspond to the two basic oxides, ferrous oxide and ferric oxide respectively. They may be illustrated by the two sulphates.

I. Ferrous sulphate. (SYNONYMS: *green vitriol, copperas.*) EXPERIMENT 295. **The properties of ferrous sulphate.** This salt is made

in large quantities by exposing iron pyrites (FeS_2) to the combined action of air and moisture, and treating the product, which contains free acid, with scrap iron. The salt is then crystallized from water. On the small scale it is made by dissolving iron in diluted sulphuric acid (Expt. 78).

Ferrous sulphate easily yields hydrated crystals of a pale green colour which are freely soluble in water. These have the composition $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and when dried at 100° leave a residue of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. The salt is apt to become oxidized if exposed to the air in solution. If the dried salt is heated strongly in contact with air and afterwards distilled, it yields fuming sulphuric acid and ferric oxide (see 193).

The following tests should be tried :—

1. Add some solution of ammonia to a solution of ferrous sulphate. A precipitate of hydrated ferrous oxide will form; this will rapidly assume a darkened colour and ultimately become brown.

2. Add a drop or two of solution of potassium thiocyanate to a freshly prepared solution of ferrous sulphate. Notice that no deep red colour is imparted to the solution.

3. Add a little solution of potassium ferrocyanide to some ferrous sulphate. A precipitate will be formed which will be bluish white at first, but will presently become blue. [What is this precipitate?]

4. Add some solution of ferricyanide of potassium to the salt. It will give a dark blue precipitate resembling Prussian blue (see cyanides).

If a concentrated solution of ferrous sulphate is mixed with oil of vitriol, crystals are deposited which are said to consist of an anhydrous sulphate (FeS_2O_7). Ferrous sulphate does not form an alum (201), but forms double salts of the type $\text{FeSO}_4 \cdot \text{M}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, which may be regarded as hydrated ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), in which one-seventh of the water of crystallization has been replaced by the salt M_2SO_4 (see also 201).

II. Ferric sulphate. EXPERIMENT 296. **The preparation and properties of ferric sulphate** ($\text{Fe}_2(\text{SO}_4)_3$). Ferrous sulphate interacts with sulphuric acid in the presence of oxidizing agents. Thus, when a mixture of ferrous sulphate and sulphuric acid is warmed with nitric acid, ferric sulphate, nitric oxide, and water are produced :—



Dissolve ferrous sulphate and sulphuric acid, in the proportions indicated by the above equation, in some water and add a moderate

excess of nitric acid. Notice that a brown solution is formed. Apply heat; nitric oxide will be evolved, and the liquid will become yellow. When no more nitrous fumes are emitted by the liquid, the solution may be concentrated. It will yield a soluble amorphous residue which contains ferric sulphate.

If the above tests be applied to a solution of this salt, the following results will be obtained :—

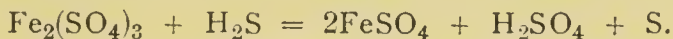
1. Alkalis will throw down a brown precipitate of hydrated ferric oxide.

2. Solution of potassium thiocyanate will give a fine crimson colouration. [What is this due to?]

3. Solution of potassium ferrocyanide will give a precipitate of Prussian blue. [What formula would you suggest for this substance?]

Pass hydrogen sulphide through an acid solution containing ferric sulphate until it smells of the gas. Notice that its yellow colour disappears and that a deposit of sulphur is thrown down; then, after boiling off excess of hydrogen sulphide, test the solution for ferrous and ferric salts as before, and also for free acid.

You will find that free acid is present, and that the ferric salt has been completely reduced. The change may be expressed as follows :—



Ferric sulphate forms several double salts. Among the most interesting of these is iron and ammonium alum (see 201) ($\text{Fe}_2(\text{SO}_4)_3, \text{Am}_2\text{SO}_4, 24\text{H}_2\text{O}$), which is used by dyers. This compound may be prepared by mixing aqueous solutions containing sulphate of ammonium and ferric sulphate in the proper proportions, and allowing the mixture to evaporate in a desiccator until it deposits lavender-coloured crystals of the alum.

The following salts of iron are important :—

500. Ferrous chloride ($\text{FeCl}_2, 4\text{H}_2\text{O}$) is a green, very soluble salt which is deposited from solutions of iron in hydrochloric acid. The anhydrous salt may be made by cautiously heating iron in dry hydrogen chloride. When heated in steam it gives off hydrogen chloride and hydrogen, leaving ferric oxide.

501. Ferric chloride (Fe_2Cl_6 , or FeCl_3). This may be made by heating iron in excess of chlorine (see 115, VI), or by oxidizing a solution of iron in excess of hydrochloric acid with nitric acid. It is a very soluble, deliquescent, crystalline solid, which is deposited

from a hot aqueous solution, on cooling, in reddish hydrated crystals. If these crystals are strongly heated they give off water and hydrochloric acid. A solution of ferric chloride in alcohol is used in medicine, under the name of 'tincture of steel.'

502. Ferrous iodide ($\text{FeI}_2 \cdot 5\text{H}_2\text{O}$) is a pale green salt which may be made by digesting iodine and iron with water and evaporating the solution. Like the other ferrous compounds it is readily oxidized. A solution of this salt together with sugar is known in pharmacy as 'syrup of iodide of iron.'

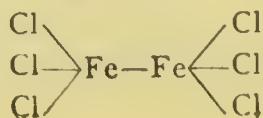
503. Iron and sulphur. **Ferrous sulphide** (FeS). This substance is used extensively for making hydrogen sulphide (183). It may be obtained by holding a rod of intensely heated iron against a lump of sulphur over some water. Drops of the molten sulphide then fall into the water and solidify, forming metallic-looking masses. Iron sulphide is apt to contain metallic iron, hence hydrogen sulphide made from this substance is usually contaminated with hydrogen (see also 459).

Iron disulphide or **iron pyrites** (FeS_2) occurs as *mundic* in crystals belonging to the regular system (339), and also as *marcasite* in trimetric crystals. It is used, as already stated, as a source of sulphur, and in the making of sulphur dioxide. When finely divided it oxidizes very rapidly with a notable rise of temperature.

504. Ferrous carbonate occurs in nature and forms a source of the metal (487). It occurs frequently in mineral waters, being held in solution by excess of carbon dioxide. Such waters are readily recognized by their chalybeate taste, and by the deposits of rust which they throw down.

Prussian blue. See 499.

505. The valency of iron. Iron, as we have seen, yields two chlorides whose simplest formulæ may be written FeCl_2 , ferrous chloride, and FeCl_3 , ferric chloride. If these formulæ be molecular formulæ, it would follow that iron can exhibit both even and uneven valency. The existence of two such chlorides can, however, be accounted for by supposing that the atom of iron is quadrivalent, and that two atoms of iron are present in each molecule of ferric chloride, as indicated by the following graphic formula:—



The vapour density of ferric chloride at temperatures below 450° supports this view, but at 750° its vapour density agrees with the simpler formula FeCl_3 .

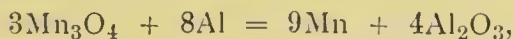
A method of measuring the proportion of iron in its ores or salts will be found in 517.

MANGANESE (Mn): Atomic weight, 54.6.

506. Manganese is abundant in nature as oxide. It often occurs in the ashes of plants.

The chief minerals which contain manganese are *pyrolusite* (MnO_2), *braunite* (Mn_2O_3), and *manganese spar* (MnCO_3). The metal, or rather a carbide analogous to cast iron, may be obtained by reducing the oxide with charcoal at a high temperature. Manganese is of a greyish-white colour, its density is 7.4, it is brittle and very prone to undergo oxidation. It dissolves in diluted mineral acids, with an evolution of hydrogen, yielding manganous salts; its salts usually exhibit a pale pink colour. Its most important alloys are *spiegeleisen* and *ferro-manganese* (see 493).

EXPERIMENT 297. A small quantity of manganese may be made from the red oxide by the action of powdered aluminium. About 100 grams of a mixture of the red oxide (made by igniting manganese dioxide) with aluminium in proper proportions * :—



is tightly packed into a crucible *A* of suitable size; this is placed in a box of sand as in Fig. 141. A thin layer of a mixture of equal weights of potassium permanganate and powdered aluminium is placed at *B*, and a short length of magnesium wire *C* is fixed in its centre. The magnesium is ignited. As soon as the action is started the lid is placed on the crucible and at once covered with plenty of sand. If the crucible is broken when cold, it will be found to contain a mass of manganese.

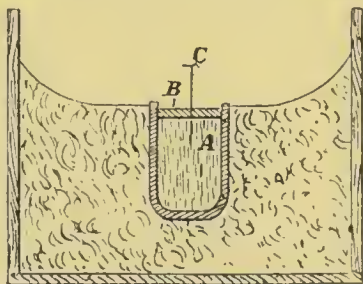


Fig. 141.

507. Manganous oxide (MnO) is difficult to obtain in the anhydrous state, for, like the corresponding oxide of iron, it is

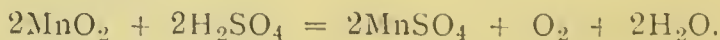
* Rather less than the theoretical proportion of aluminium should be used.

rapidly oxidized by atmospheric air; but it may be made as a greenish powder by heating manganous carbonate or manganous oxalate in hydrogen gas. The corresponding hydroxide falls as a white precipitate when an alkali is added to a solution of a manganous salt, but this rapidly absorbs oxygen, turning brown. (Compare ferrous hydroxide, 499, 1.) It is a basic oxide, and most of the salts of manganese correspond to this oxide.

508. Trimanganous tetroxide (Mn_3O_4) occurs native. It is a basic peroxide (see 120).

509. Manganic oxide or manganese sesquioxide (Mn_2O_3). This occurs in nature as *braunite*; and it is said to be formed when the dioxide is strongly heated. A manganic hydroxide ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is known. The manganic salts (MnR'_3 or $\text{Mn}_2\text{R}'_6$) are chiefly known in the form of double salts. Thus there is a stable alum having the composition $\text{K}_2\text{SO}_4, \text{Mn}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$: and some double chlorides containing manganic chloride have recently been prepared. It is a basic peroxide.

510. Manganese dioxide or black oxide of manganese (MnO_2). This oxide occurs as *pyrolusite*, and is formed when manganese nitrate is heated cautiously. When strongly heated it evolves oxygen, leaving a residue of Mn_3O_4 or of Mn_2O_3 , and it was formerly recommended as a source of that gas. When heated with sulphuric acid, or with hydrochloric acid, it yields manganous salts, together with oxygen or chlorine, according to the nature of the acid employed. Thus, with the former acid, the action corresponds to the following equation:—



It is, therefore, a basic peroxide. It can, however, form compounds with basic oxides; thus we meet with the compound CaO, MnO_2 in the 'Weldon process' (139).

511. Manganous sulphate is used extensively by calico printers, and can be prepared as described above. If a solution of the salt be crystallized at ordinary temperatures the crystals are isomorphous with those of copper sulphate, and have the composition $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. At low temperatures the solution deposits crystals which have the composition $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$, and are isomorphous with green vitriol, and another hydrate $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ also exists.

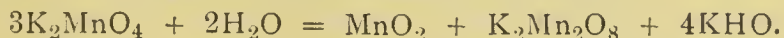
512. Manganic sulphate is only stable in the form of the alum alluded to above.

513. Manganous chloride (MnCl_2). This salt is left in solution when manganese dioxide is heated with hydrochloric acid; it can be obtained in pink crystals which have the composition $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. The anhydrous salt is colourless.

514. Manganic chloride (MnCl_3 or Mn_2Cl_6). This compound has been obtained in the form of double salts, having the composition $2\text{KCl} \cdot \text{MnCl}_3 \cdot \text{H}_2\text{O}$, and $2\text{NH}_4\text{Cl} \cdot \text{MnCl}_3 \cdot \text{H}_2\text{O}$.

515. Manganous sulphide (MnS). This is an olive-green solid; it is formed when manganese is heated in the vapour of carbon disulphide. A hydrated pale pink form of the same substance is precipitated when a solution of an alkaline sulphide is mixed with a manganous salt. It rapidly darkens in air.

516. EXPERIMENT 298. The preparation of potassium manganate and permanganate. 1. Mix manganese dioxide 2 parts; caustic potash, in solution, 2 parts; and potassium chlorate, 1 part. Evaporate the mixture to dryness, and heat it rather strongly in the air. Allow the product to cool and throw it into cold water. A deep green solution containing potassium manganate (K_2MnO_4) will be formed, and if this solution be evaporated *in vacuo*, it will yield dark green crystals of the potassium manganate. This salt is soluble in water containing free alkali, but if it be added to water and exposed to the air, or heated, it yields manganese dioxide, potash, and potassium permanganate which remains in solution:—



Solutions of sodium manganate are largely used as disinfectants.

2. **Permanganic acid and potassium permanganate.** If the solution of potassium permanganate obtained as described above is concentrated it yields a crop of dark iridescent crystals of potassium permanganate ($\text{K}_2\text{Mn}_2\text{O}_8$ or KMnO_4) which are isomorphous with potassium perchlorate (see 153). This beautiful salt is very largely used as a disinfectant, and as an oxidizing agent.

Permanganic Acid. If potassium permanganate be added cautiously to a well cooled mixture of sulphuric acid and water in molecular proportions in a test tube, and heated to 60° or 70° it evolves violet vapours, which may consist of permanganic acid ($\text{H}_2\text{Mn}_2\text{O}_8$), or of its

anhydride (Mn_2O_7). These may be condensed to a dark green hygroscopic liquid which possesses great oxidizing power. As it is explosive it should only be made in very small quantities and with great care.

EXPERIMENT 299. The properties of potassium permanganate.

1. Add some dilute solution of potassium permanganate gradually to some water containing a trace of organic matter * and acidulated with dilute sulphuric acid. The colour of the permanganate will be destroyed.

2. Pass hydrogen sulphide slowly through some solution of potassium permanganate acidulated with dilute hydrochloric acid. Notice that the colour of the permanganate disappears, that sulphur is deposited, and that the solution obtained gives the reactions of a salt of manganese.

3. Repeat the last experiment, using sulphur dioxide or solution of sulphurous acid (H_2SO_3), instead of hydrogen sulphide. An analogous result will be obtained, the sulphurous acid being oxidized at the expense of the permanganate.

4. Make similar experiments using other reducing agents; for example, with oxalic acid.

5. Examine the action of hydrogen and sodium peroxides on the permanganate.

The student should endeavour to express the changes observed in the above experiment by equations, and submit these equations to his teacher for correction.

517. The oxidizing power of potassium permanganate is made use of in quantitative analysis. Unfortunately, solutions of this salt become gradually weaker when kept, and therefore their oxidizing power must be remeasured at frequent intervals.

EXPERIMENT 300. To titrate a solution of permanganate of potassium by means of ferrous sulphate. Before doing this experiment, read again the sections on alkalimetry in 116.

Dissolve about 5 grams of potassium permanganate in a little water: dilute the solution to 1 litre, and standardize it by means of a freshly prepared solution of ferrous and ammonium sulphate as follows:—

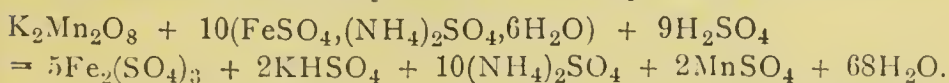
Dissolve exactly 7 grams of ferrous and ammonium sulphate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) in some recently boiled distilled water, and make up the solution to 250 c.c.

Fill a burette with some of the oxidizing solution. Allow it to flow into a flask containing 30 or 40 c.c. of the solution of iron and am-

* Such as a dilute vegetable extract.

monium sulphate, together with some diluted sulphuric acid (see equation below), until the liquid acquires a faint permanent pink colour. Observe what volume of permanganate has been employed.

The following equation expresses the action of the permanganate with the ferrous salt in the presence of free sulphuric acid :—



Let us suppose that 250 c.c. of the iron solution contained 7 grams of ferrous and ammonium sulphate, that x c.c. of this solution was taken, and that it decolorized x c.c. of the permanganate solution.

Then $\frac{7 \times x}{250}$ grams of the ferrous salt are equivalent to the permanganate of potassium contained in x c.c. of the solution of that salt.

But one molecular proportion of permanganate ($\text{K}_2\text{Mn}_2\text{O}_8$) (molecular weight = 316) will oxidize ten molecular proportions of ferrous and ammonium sulphate (molecular weight = 392).

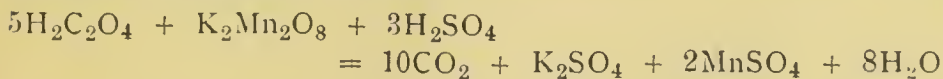
Let y be the mass of permanganate in x c.c. of the solution. Then, to find the value of y , we have—

$$(392 \times 10) : 316 :: \frac{7 \times x}{250} : y.$$

And $\frac{y}{x}$ will give us the amount of permanganate in each c.c. of the solution.

With the aid of the above general explanation and his previous experience the student should be able to work out the results of his titrations, and to carry out the following exercises.

EXPERIMENT 301. To find the percentage of oxalic acid in crystals of oxalic acid. Calculate, from the following equation and from the data obtained in the previous experiment, how much oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) will be oxidized by each cubic centimetre of your standard permanganate solution :—



Example. Let the mass of permanganate in each cubic centimetre of the solution be M , and let the unknown weight of oxalic acid be x .

Then, since $\text{K}_2\text{Mn}_2\text{O}_8 = 316$ and $5\text{H}_2\text{C}_2\text{O}_4 = 450$,

$$316 : 450 :: M : x.$$

Dissolve a suitable quantity of freshly crystallized oxalic acid (dried by pressing it between sheets of bibulous paper) in water; add

a sufficient quantity of sulphuric acid, dilute the solution to 100 c.c., 200 c.c., or some other convenient volume, and titrate measured portions of this solution with the permanganate solution.

Let us suppose that N grams of the crystals of oxalic acid are dissolved in 100 c.c. of water, and that 10 c.c. of the solution are oxidized by 40 c.c. of the permanganate solution.

Then, since 1 c.c. of permanganate will oxidize x grams of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), 40 c.c. will oxidize $40x$ of oxalic acid.

Therefore $\frac{N}{10}$ of crystallized oxalic acid contains $40x$ of real oxalic acid, and $\frac{N}{10} - 40x$ of water.

The results obtained should be stated as percentages.

We have seen that iron in the ferrous state may be estimated by means of a standard solution of potassium permanganate. The same reagent may be used to determine iron in the ferric state if the latter is first reduced.

Obtain some solution of ferric sulphate of known concentration, and ascertain its strength in the following manner:—

Place a measured volume of the ferric solution in a flask, add ammonium hydroxide until it is very slightly alkaline, place a funnel in the mouth of the flask, add solution of ammonium bisulphite*, and heat gradually to boiling until the yellow colour of the liquid has disappeared, and until the salt is wholly dissolved. If the solution should bump during this process, throw in a few scraps of platinum wire. Then add diluted sulphuric acid in sufficient quantity to decompose the excess of sulphite (30 c.c. of a solution containing 1 part of acid to 2 parts of water will be sufficient for 5 c.c. of the solution of bisulphite); boil until all the sulphur dioxide is expelled; dilute with boiled water to a fixed volume; test for ferric salts with potassium thiocyanate, and if none be present titrate measured portions of the solution with permanganate as before, and as quickly as possible.

Finally, calculate the amount of ferric sulphate present in the solution.

Sulphuric acid must be used in the above experiments.

Manganese may be recognized in solutions of its salts by adding

* If this be made by saturating strong solution of ammonia with sulphur dioxide, about 5 c.c. may be added for each gram of the iron salt.

ammonia and ammonium sulphide, which produce the characteristic flesh-coloured sulphide. Also by the production of a green mass, which contains a manganate, when a fragment of the salt is fused with nitre. If salts of manganese are heated with borax in the outer flame of a blow-pipe they give an amethyst-coloured bead, which becomes colourless in the inner flame.

518. Certain of the compounds of manganese, the permanganates, are isomorphous with the corresponding perchlorates and periodates, and manganese is sometimes placed in the seventh group (see p. 181).

COPALT AND NICKEL.

519. These two metals, which are usually found together and are separated with difficulty, have atoms which differ but little in weight. They are distinguished for the beautiful colours of their salts; both are more fusible than iron and both are magnetic; both exhibit tenacity, malleability, and ductility in a marked degree, and they are much less apt to be corroded by moist air than iron.

In order to separate them, the native oxide, or sulphide, is roasted to expel arsenic and sulphur, and then extracted with solution of hydrochloric acid. The solution is diluted and mixed with bleaching powder and milk of lime in suitable proportions to precipitate oxide of iron and arsenic. The liquid is separated from the precipitate and treated with hydrogen sulphide to throw down copper, lead, bismuth, and any remaining arsenic. The cobalt is then removed as oxide, by heating the solution and adding more bleaching powder. The nickel is afterwards precipitated by milk of lime. The oxides may be reduced by heating them with carbon.

A very interesting process for separating nickel from cobalt has been introduced lately; it is based on the discovery, by Dr. Mond, that freshly reduced nickel combines with carbon monoxide below 150° , forming a remarkable compound called *nickel carbonyl* ($\text{Ni}(\text{CO})_4$). Iron, alone of the other metals, forms a similar compound, but iron does not combine with carbon monoxide very freely, and therefore it is possible to separate nickel from all the other metals by a single operation by taking advantage of this property.

In the 'carbonyl process' the ore is thoroughly roasted, reduced at 400° by the action of water gas (Expt. 219, 4), and exposed to the action of a current of carbon monoxide in chambers heated to about 80° .

The carbon monoxide leaves the chambers charged with nickel carbonyl, and is carried through tubes heated to 180° to decompose the latter compound. The nickel is deposited in the tubes, and the liberated carbon monoxide may then be used again.

COBALT (Co): Atomic weight, 58.56.

520. This metal is white, highly tenacious and volatile; its density is about 8.7. Its melting-point is but little below that of iron. It is less readily attacked by hydrochloric acid and sulphuric acid than iron, and is permanent in atmospheric air.

Cobalt forms two classes of salts corresponding to the ferrous and ferric salts of iron, but the cobaltic salts are most of them unstable.

521. Cobaltous oxide (CoO). This is a grey powder which is soluble in acids. Its salts exhibit a beautiful red colour when hydrated, but are blue when anhydrous. It may be made by adding sodium carbonate to a solution of cobalt nitrate, or sulphate, and cautiously igniting the washed and dried precipitate out of contact with air. It is readily reduced by hydrogen. The hydroxide is precipitated by ammonia, but it is soluble in excess, and in ammonium chloride. The most important cobaltous salts are the chloride and sulphate.

522. Cobaltous chloride (CoCl_2). This salt may be prepared by dissolving cobaltous oxide in hydrochloric acid, when it forms a fine red solution, which deposits the salt in red hydrated crystals ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). There is also a dihydrate, and a monohydrate ($\text{CoCl}_2 \cdot \text{H}_2\text{O}$) which is violet in colour. If the solution be concentrated and mixed with strong solution of hydrochloric acid it gradually assumes a deep blue colour. The anhydrous salt is blue.

If some characters are written on paper with a dilute solution of cobalt chloride, and exposed to a fire, they soon exhibit a deep blue colour, which fades in damp air, but can be reproduced by warming.

Cobaltous bromide (CoBr_2) and iodide (CoI_2) are also known. The latter is black when anhydrous, but in air it becomes moss green ($\text{CoI}_2 \cdot 2\text{H}_2\text{O}$), and finally pink ($\text{CoI}_2 \cdot 6\text{H}_2\text{O}$).

523. Cobaltous sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) is a red, moderately soluble salt, which is isomorphous with green vitriol ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

524. Cobaltic oxide (Co_2O_3). If a solution of freshly made chloride of lime (see 150) be added to a solution of cobalt chloride,

a precipitate of hydrated cobaltic oxide will fall. This dissolves in acids, forming instable cobaltic salts.

Cobalt also yields an oxide Co_3O_4 , and a dioxide CoO_2 .

The oxides of cobalt are remarkable for their power of imparting a blue colour to borax beads and glass. This property is made use of by the makers of coloured glass, and by chemists in testing for cobalt. *Smalt*, the pigment, consists of a glass coloured by oxide of cobalt and finely powdered.

The salts of cobalt form a number of interesting compounds with ammonia, but the student must consult a larger treatise on chemistry if he desires to become acquainted with these compounds.

NICKEL (Ni) : Atomic weight, 58.3.

525. The method of separating this metal from its ores has already been described. Small quantities may be made by reducing the oxide with hydrogen.

Nickel is white, malleable, ductile, and exhibits metallic lustre. Its density is 8.3; after it has been rolled and stamped it is about 8.8. Its melting-point is nearly as high as that of iron. It is magnetic, but loses this property when heated. It is used extensively for plating iron, as it takes a bright polish and is not easily corroded by air.

Alloys of nickel with copper or zinc, and sometimes nickel itself, are used in some countries for coins. 'German silver' is such an alloy. Owing to their hardness nickel coins wear well, and, owing to the value of the metal, nickel coins of a given denomination are smaller than copper coins of corresponding value.

Silver-plated goods are often made of alloys of nickel.

526. Nickel monoxide (NiO). This is formed by heating nickel nitrate or carbonate to redness, or by adding alkali to a solution of a nickel salt, and igniting the hydrated oxide. It is a grey or greenish powder, which dissolves in acids giving green solutions. When these solutions are evaporated they deposit green hydrated crystals. Nickel hydroxide (NiH_2O_2) is soluble in ammonia.

527. Nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) may be made as described in the previous paragraph. It forms beautiful emerald green crystals, isomorphous with magnesium sulphate, and yields double salts which contain only six molecules of water of crystallization, e.g. $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$; $\text{NiSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (see 201). The former is used in plating with nickel.

Other salts corresponding to this oxide, such as the nitrate, which is soluble, and the carbonate and oxalate, which are insoluble, can also be obtained. The latter when heated to a white heat yields metallic nickel.

528. Nickel sesquioxide (Ni_2O_3) may be obtained by adding excess of alkali to a solution of a nickel salt and passing a stream of chlorine through the liquid in which the precipitated hydroxide of nickel is suspended. It is a black powder which evolves oxygen when heated, and which evolves chlorine when warmed with hydrochloric acid. The corresponding salts are unstable.

Nickel gives a green precipitate of hydroxide of nickel with ammonium hydroxide, which is soluble in excess of the reagent. The carbonate is easily decomposed by heat. Hydrogen sulphide gives no precipitate with salts of nickel in the presence of mineral acids, but ammonium sulphide throws down a black precipitate of nickel sulphide from neutral or alkaline solutions. A little of the sulphide is apt to remain dissolved, forming a dark solution, if excess of the ammonium sulphide be used.

CHAPTER XXXIII

COPPER (Cu): Atomic weight, 63.1.

Copper is placed in Group I, and also in Group VIII in the table on p. 181. When studying this metal the student should endeavour to discover why this is done.

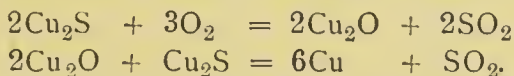
529. The ores of copper. Metallic copper is sometimes found in large masses, and when native it generally presents a curious branched appearance. It is found in 'faults' in the granite in Cornwall and elsewhere. On the shores of Lake Superior masses of pure copper weighing as much as 400 tons have been met with.

The most abundant ore of copper is *copper pyrites*, which consists of the sulphides of copper and iron ($\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3$). It is also found as cuprous oxide (Cu_2O) in *red copper ore*; as cupric oxide (CuO); as a basic carbonate ($\text{CuCO}_3, \text{CuH}_2\text{O}_2$) in *malachite*, which is green, and also in *blue malachite* ($2\text{CuCO}_3, \text{CuH}_2\text{O}_2$); and associated

with sulphur, iron, antimony, arsenic, and sometimes with silver and zinc, in *grey copper ore*, which is abundant and important.

530. Extracting copper from its ores. In the Welsh process a suitable mixture of ores is roasted in a reverberatory furnace. This oxidizes iron and removes some sulphur and arsenic, but leaves most of the copper in combination with sulphur. The roasted material is then fused with ore containing silica, and with fusible slags, and the mixture separates into an upper layer consisting of slag which contains much of the iron as silicate, and a lower layer of impure sulphide of copper. The latter is run into water to granulate it. The crude copper sulphide thus obtained is called 'coarse metal'; it is again roasted, and then remelted together with suitable slags, after adding ores containing oxide and carbonate of copper. After about six hours the copper sulphide can be drawn from under the fused slag in a comparatively pure state. The product at this stage is known as 'fine metal.'

At the next stage the cuprous sulphide is roasted in order to convert part of it into oxide, and then heated to such a degree that the contents of the furnace melt; the oxide then interacts with unoxidized sulphide, and produces sulphur dioxide, which escapes, and metallic copper which subsides and is afterwards run into moulds. These reactions are sometimes written thus :—



Copper is sometimes extracted from spent pyrites (see 194) by roasting it with salt, treating the product with water to extract the copper chloride, and placing scrap iron in the solution to displace the copper.

531. Refining crude copper. The pigs of copper produced as above described still contain sulphur and arsenic, and also metallic impurities. They are piled in a furnace and roasted to oxidize these impurities; then melted, and, after a thin layer of slag has been removed, are covered with powdered charcoal and stirred with poles of young wood until the metal has a proper colour and structure. During this final stage, any oxygen that may have been taken up in the previous process is removed.

Copper may be refined electrolytically (see Expt. 255) by suspending bars of crude copper and sheets of refined copper near one another in a solution of copper sulphate. The former are connected to the anode and the latter to the kathode of a dynamo, and a current is

passed between them. When this is done the copper gradually passes into solution and is redeposited at the kathode, whilst the impurities fall to the bottom of the vessel or remain dissolved.

532. The properties of copper. The qualities of copper depend, to a great extent, upon its purity. Sulphur and antimony, which are often present, reduce its tenacity and malleability, but arsenic is less injurious in these respects. Pure copper conducts electricity almost as well as silver (126), but some samples of Spanish copper, which contain arsenic, have only about one-seventh the conducting power of the pure metal. Copper, as is well known, has a reddish-yellow colour, and its density is nearly 9.0 (water = 1). It is readily drawn into wire, may be beaten into thin sheets, and it is a good conductor of heat. It melts at about 1050° , and is probably slightly volatile at very high temperatures.

Alloys of copper are largely used. Thus brass, bronze, speculum metal, and gun-metal all contain copper, and it is used to harden gold and silver coin.

Copper is probably not affected by pure dry air, but if it be exposed to moist air it becomes covered with a green crust which evolves carbon dioxide when treated with acids. It is attacked by hot, strong sulphuric acid (see 187), and by nitric acid of various degrees of concentration (see 239), but not readily by dilute sulphuric or hydrochloric acid. Carefully dried chlorine does not attack copper, but if moisture be present they combine readily. It forms cupric oxide (CuO) if strongly heated in air or oxygen.

533. Copper hydride (Cu_2H_2). This compound is formed when cupric sulphate is warmed with a solution of hypophosphorous acid. It dissolves in hydrochloric acid, although metallic copper will not do so.

534. Copper forms two basic oxides, cuprous oxide (Cu_2O) and cupric oxide (CuO), and a sub-oxide (Cu_4O) and dioxide (CuO_2) are also said to exist.

535. Cuprous oxide, red oxide of copper (Cu_2O). EXPERIMENT 302. Dissolve a few grams of copper sulphate in water, add some grape sugar, then excess of potash, and heat the mixture. The sub-oxide of copper (Cu_2O) will be deposited as a red powder.

Add some of the oxide to some strong solution of hydrochloric acid. It will dissolve, forming cuprous chloride (Cu_2Cl_2). Notice that the solution is not blue or green.

Warm a little cuprous oxide with some sulphuric acid. Notice that a cupric salt is formed, and that an insoluble residue is left. If you examine this residue you will find that it consists of metallic copper.

[How would you expect cuprous oxide to behave with nitric acid?]

Cuprous oxide occurs in nature as red copper ore (529). It is used for imparting a red colour to glass.

536. Cupric oxide, black oxide of copper (CuO). This oxide, which occurs native, may be made by igniting nitrate or carbonate of copper, or by roasting the metal in air.

Cupric hydroxide. Add solution of soda or potash to some solution of copper sulphate. The bulky pale blue precipitate which forms is cupric hydroxide ($\text{Cu}(\text{H}_2\text{O})_2$). Heat the precipitate in its mother liquor to the boiling-point, and notice that it changes quickly into the black oxide of copper :—



Warm some cupric oxide with diluted sulphuric or hydrochloric acid, decant the solution, concentrate and allow it to cool. Crystals of copper sulphate or chloride will form. In these experiments no oxygen or chlorine is evolved, therefore cupric oxide is a basic oxide. Cupric oxide is not decomposed at a red heat, but it is easily reduced.

The following are among the most important copper salts.

537. Cuprous chloride (Cu_2Cl_2). A solution of this salt can be produced as described in 535; it can be obtained also by reducing a solution of cupric chloride with stannous chloride; if sufficiently diluted the solution yields a colourless precipitate of cuprous chloride. It is gradually oxidized by air in the presence of hydrochloric acid.

For its use in gas analysis, see Experiment 241.

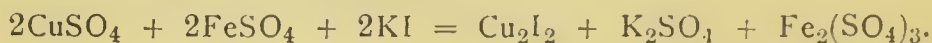
538. Cuprous iodide (Cu_2I_2). EXPERIMENT 303. Add some solution of potassium iodide to half a gram of cupric sulphate dissolved in water. Collect the precipitate which falls, and warm the filtrate. The vapour of iodine will be given off, for the following reaction occurs :—



Repeat the experiment, but replace the solution of cupric sulphate by one containing a mixture of 1 part of cupric sulphate and at least $2\frac{1}{3}$ parts of ferrous sulphate.

Cuprous iodide will again be precipitated, but, if sufficient ferrous

sulphate has been used, no iodine will be liberated. On the other hand, plentiful evidence that a ferric salt has been formed will be obtained, if suitable tests are applied (see 499). The following equation represents the change :—

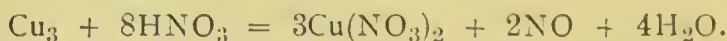


539. Cupric sulphate, blue vitriol ($\text{CuSO}_4, 5\text{H}_2\text{O}$). This salt is a by-product in the preparation of sulphur dioxide (187).

It may be made by roasting scrap copper or copper sulphide in air, digesting the oxide formed in sulphuric acid, and crystallizing it from water. Copper sulphate is apt to contain traces of ferrous sulphate. These cannot be removed by recrystallizing the salt; but if it be warmed with nitric acid, the ferrous sulphate is converted into ferric sulphate, and the solution will afterwards yield crystals of blue vitriol free from iron.

When crystallized copper sulphate is heated to 100° it loses four-fifths of its water, and the residue has the composition $\text{CuSO}_4, \text{H}_2\text{O}$. The last molecule of water is much more difficult to remove (see 201). It forms compounds with the sulphates of potassium and ammonium analogous to those formed by magnesium. If copper sulphate be very strongly heated it yields cupric oxide, sulphur dioxide, and oxygen. The monohydrated copper sulphate ($\text{CuSO}_4, \text{H}_2\text{O}$) readily reabsorbs water, and hence affords us a useful test for this substance.

540. Cupric nitrate ($\text{Cu}(\text{NO}_3)_2, 3\text{H}_2\text{O}$). This salt remains in solution in the making of nitric oxide (239) :—



When heated strongly it yields a residue of copper oxide, and gives off red fumes which contain nitrogen peroxide (NO_2).

Cupric nitrate is a very corrosive substance. If a crystal of it be rapidly rubbed with tinfoil, the latter is attacked so violently that it becomes incandescent.

541. Cupric carbonates. These are chiefly basic compounds. One of the best known is *malachite* ($\text{CuCO}_3, \text{CuH}_2\text{O}_2$), and blue malachite ($2\text{CuCO}_3, \text{CuH}_2\text{O}_2$) is also known.

542. Cuprous sulphide (Cu_2S) occurs native, and cupric sulphide may be prepared by the action of hydrogen sulphide on solutions of cupric salts.

543. Cupric chloride (CuCl_2). If copper leaf is thrown into

chlorine the two elements combine, with incandescence, yielding a yellowish residue of cupric chloride.

If cupric oxide is heated with strong solution of hydrochloric acid it forms a yellow solution; if this is gradually diluted with water, it becomes green, and on further dilution, blue. The salt may be obtained in pale blue crystals having the composition $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

544. Cupric arsenite (CuHAsO_3) is the fine green pigment known as 'Scheele's green.' It is easily made by mixing a solution of cupric sulphate with an alkaline arsenite. This salt was formerly much used for colouring wall-papers; it is not, however, suitable for the purpose, owing to its highly poisonous character.

The most important silicates of copper are *chrysocolla* ($\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$) and *diopside* ($\text{CuSiO}_3 \cdot \text{H}_2\text{O}$). They occur in Cornwall and elsewhere.

Copper may be recognized in its compounds by the blue colour of the hydrated cupric salts, and by the deep-blue compounds which these form with ammonia. If a copper salt moistened with strong hydrochloric acid is held in the Bunsen flame a fine green colouration with a blue centre is communicated to the flame. In the absence of halogens the colouration is green. The cuprous salts and the anhydrous cupric salts are not blue, but they may be recognized easily by the other tests mentioned.

If a borax bead containing a copper salt is heated in the oxidizing blow-pipe flame, the bead becomes green whilst hot, but assumes a blue colour when cold. Red streaks are produced if the bead is heated in the reducing flame with fragments of tin. When compounds of copper are heated on charcoal with potassium cyanide they yield spangles of metallic copper.

Solutions containing salts of copper give precipitates of the sulphide with hydrogen sulphide in the presence of free acid, and ammonium sulphide gives similar precipitates with neutral solutions. Copper sulphide is insoluble in alkaline sulphides. The action of alkalis on copper salts has already been described.

The compounds of copper are irritant poisons. Therefore copper vessels intended for domestic use should be tinned internally. Vegetable juices or extracts should never be allowed to stand in untinned copper vessels, and food containing vinegar should never be prepared in them.

CHAPTER XXXIV

SILVER (Ag): Atomic weight, 107.12.

545. SILVER was known to the alchemists as *luna*, the moon, and silver nitrate (AgNO_3) is still called *lunar caustic*.

Silver is found in the metallic state, sometimes alloyed with gold and occasionally with mercury; also as sulphide (Ag_2S) in *silver glance*, and in *ruby silver* ($3\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$). It occurs combined with chlorine in *horn silver* (AgCl), occasionally as bromide or iodide, and in *argentiferous galena* (444).

The proportion of silver in its ores is usually small, and it is often found in districts where fuel is scarce, hence it is not prepared by smelting the ores at high temperatures.

The Mexican amalgamation process. This process depends on the production of silver chloride, which is afterwards reduced by the action of mercury. For this purpose, the ore is sorted, crushed to a mud with water, mixed with from 1 to 5 per cent. of common salt, and left for some hours. Then some copper sulphate (magistral) is added; the whole is well trampled repeatedly with quicksilver* by mules, and allowed to stand for a fortnight. More quicksilver is added, gradually, and the mixture stirred up with running water which carries off most of the earthy matter and leaves an amalgam of mercury and silver. The mercury is recovered from the amalgam partly by straining, and partly by distilling the residue after straining it. It is supposed that in this process the copper sulphate and common salt form cupric chloride (and some cuprous chloride) and sodium sulphate; that the chloride of copper and the sulphide of silver interact, producing chloride of silver, and that this is reduced by part of the mercury:—



Refractory ores are roasted with salt to produce silver chloride, which is then reduced by a method more or less resembling that just described, or by churning it up with water and scrap iron to reduce the silver chloride, and with mercury to dissolve the silver from the accompanying impurities.

Extracting silver from lead. *Desilverizing lead.* Unless the lead is highly argentiferous it is first treated as follows:—

* About one part of mercury is added for every two parts of silver in the ore.

Pattinson's process or the method of eighths. A series of, let us say, four melting-pots having been set up, several tons of argentiferous lead are melted in the first pot, and allowed to cool until crystals appear. These crystals, which consist of lead, are transferred with some adherent liquid metal to pot 2, by means of a perforated iron ladle, until only a fourth of the lead originally taken remains in pot 1. Half the residue also is removed to be remelted in pot 1, and the last eighth, which is comparatively rich in silver, is cast into ingots.

The one-eighth part reserved for remelting in pot 1 is richer in silver than that placed in pot 2, but poorer than the ingots. It is remelted with a fresh supply of lead and treated as before.

The impoverished lead in pot 2 is treated similarly, six-eighths of it being transferred to pot 3, one-eighth reserved for remelting in pot 2, and the remaining eighth placed in pot 1. The contents of pot 3 are then treated in the same way.

When the contents of a pot contain sufficient silver the lead is cupelled. That is to say, it is exposed, at a high temperature, in a very shallow crucible made of compressed bone-earth (248), to a strong current of air. When thus treated the lead is rapidly converted into oxide, which is partly removed from the surface of the remaining metal by blasts of air, and partly absorbed by the porous cupel. Towards the end of the process a beautiful play of colours may be seen on the surface of the metal, and when the last film of oxide has been removed a splendid surface of molten silver appears *. If the cooling silver is watched till a thin crust has formed upon it, the molten metal will be seen to burst forth from numerous craters, and when it is solid, its surface will present a highly irregular and very beautiful appearance. This curious phenomenon is due to the fact that molten silver occludes oxygen, which escapes again as the metal approaches its solidifying point.

The Parkes process, which has now replaced the Pattinson process in some districts, depends on the fact that a molten mixture of lead and zinc forms separate layers on cooling, and that silver forms alloys with zinc more readily than with lead. Melted argentiferous lead, nearly free from arsenic and antimony, is well mixed with zinc, and the mixture is allowed to cool. During cooling, crusts of zinc, which contain most of the silver, form, and are removed by skimming. These crusts are distilled, and leave a residue of silver and lead which is afterwards cupelled.

* This is called brightening.

On account of its softness, silver is generally hardened by adding copper. The hardest alloy contains 20 per cent. of copper, but the proportion used in British coinage is about $7\frac{1}{2}$ per cent. On the Continent 10 per cent. of the baser metal is employed. The copper also deprives the silver of its power of occluding oxygen, and thus gives us a material which may be used for taking castings.

The density of an English silver coin is 10.3, that of pure silver is 10.5. Silver melts at a bright red heat, it is highly malleable and ductile, and is an excellent conductor of heat and electricity. It is quite unalterable in pure air at all temperatures, but is blackened by contact with alkaline sulphides. It dissolves but slightly in hydrochloric acid, but it is attacked by hot sulphuric acid, and by nitric acid. With the former it yields sulphur dioxide (187) and sulphate of silver. With the latter it produces nitrate of silver and nitrous fumes. The action of nitric acid on silver is very slight if the acid is free from the lower oxides of nitrogen, and its solvent power is greatest if it be moderately diluted with water. Silver may be extracted from its alloys by dissolving them in nitric acid, which leaves behind gold, if any be present, adding solution of common salt, collecting the precipitate of silver chloride, washing it with water, and heating it strongly with purified carbonate of sodium:—



Frosted silver is made by heating standard silver in the presence of oxygen till a film of oxide of copper has formed on its surface. It is then treated with dilute sulphuric acid, or with solution of ammonia: this removes the oxide, and leaves a lustreless surface of pure silver.

Oxidized silver (so called) is silver coated with a thin film of sulphide by immersing it in a bath containing sulphide of potassium.

Electroplating with silver was described in 341.

546. Allotropic silver. If a mixture of ferrous sulphate and sodium citrate is added to an ammoniacal solution of silver nitrate, in proper proportions, the solution reddens and deposits a precipitate which may resemble gold or exhibit a bluish-green colour. It is readily converted into ordinary silver by friction or by contact with acids. This precipitate has been supposed to be an allotropic form of silver, but the most recent research does not support this conclusion.

547. Argentic oxide (Ag_2O). Add a little potash or soda to solution of silver nitrate, collect, and wash the precipitate:—



Argentio oxide is a dark-brown powder, very slightly soluble in water, yet sufficiently so to turn damp red litmus paper blue. It absorbs carbon dioxide from the air when moist. If it be heated moderately it is resolved into oxygen and metallic silver.

The other chief oxide of silver, the dioxide (Ag_2O_2), is a basic peroxide (see 120); it is formed by the electrolysis of a strong solution of silver nitrate.

548. Argentio chloride (AgCl), *horn silver*. This salt occurs native in parts of America, in Siberia, Norway, Germany, and elsewhere. It is insoluble, and therefore may be obtained as a precipitate by mixing a solution of silver nitrate with a solution of any soluble chloride. It dissolves in ammonia forming the compound $3\text{NH}_3, 2\text{AgCl}$, and, like some other silver salts, is soluble in potassium cyanide.

Fuse about a gram of chloride of silver, and allow it to cool. The product will be found to be translucent, and sufficiently soft to be cut with a knife, hence the name 'horn silver.'

549. Argentio nitrate (AgNO_3), *lunar caustic* (Exercise 1, p. 141), is a soluble, very corrosive solid, largely used as a styptic in medicine. It melts easily, and is soluble in water, alcohol, and ether. It stains the skin black, and a solution of silver nitrate, thickened with gum, is often employed for marking linen.

550. Argentio sulphate (Ag_2SO_4) is a sparingly soluble salt made by heating silver with oil of vitriol.

551. Argentio phosphate (Ag_3PO_4) is a pale yellow insoluble solid. It is formed when a solution of silver nitrate is mixed with neutral sodium phosphate (Expt. 198).

552. Argentio iodide (AgI). This salt is met with in Mexico and Chili. It may be prepared by adding a solution of a soluble iodide to a solution of a soluble silver salt in equivalent proportions. Like chloride of silver it is fusible, forming a liquid which solidifies to a yellow, translucent tough mass. It is less sensitive to light than the chloride and bromide.

553. Argentio sulphide (Ag_2S) has already been mentioned as *silver glance*. It may be made by passing hydrogen sulphide into

a solution of a salt of silver. If it is fused and then allowed to cool, it forms a soft, leaden grey mass, which can be cut easily with a knife.

554. The use of silver salts in photography. EXPERIMENT 304. Prepare a little fresh silver chloride by mixing a solution of silver nitrate with a solution of common salt. Observe that the freshly made salt is colourless, and then expose it to strong light. It will soon begin to darken, becoming first lavender, and subsequently violet. Bromide of silver behaves similarly.

The above dark compound is insoluble in a solution of sodium thiosulphate, but the unaltered silver halide is soluble, and photographers take advantage of this difference in 'fixing' their pictures. Suitable films containing silver chloride or bromide are exposed in a camera to light from the object to be photographed, and then washed with a solution of 'hypo,' to remove the unchanged halide. This leaves the darkened substance on the film so distributed as to give the 'negative,' a picture in which the darker parts of the object photographed appear light, and the brighter parts dark. By placing this above a similar film, and exposing them to daylight, a positive picture is produced on the second film, which is afterwards fixed with 'hypo' as before.

Silver in combination is recognized by the behaviour of its compounds with soluble chlorides, bromides, and iodides, and by the action of light on the chloride and bromide of silver. Its compounds are readily reduced when heated on charcoal with an alkali in the reducing part of a blow-pipe flame, or by warming an ammoniacal solution of the salt with a reducing agent such as potassium tartrate.

Silver resembles the metals of the alkalis in being univalent, and in the fact that its oxide (Ag_2O) is alkaline and absorbs carbon dioxide, though it is almost insoluble. On the other hand it exhibits the physical qualities of the typical metal much more decidedly than the metals of the alkalis. Silver is far less readily oxidized, and its oxides and the salts it forms with the oxyacids are far less stable, than those of the alkali metals. Finally its chloride, bromide, and iodide, and also carbonate, phosphate, and oxalate of silver are insoluble, though the corresponding salts of the metals of the alkalis are soluble.

CHAPTER XXXV

GOLD AND PLATINUM

GOLD (Au) : Atomic weight, 195.7.

555. THE collecting of 'gold dust' from the sands and gravels which form the beds of many rivers has long been an industry of some importance, but we obtain most of our gold from mines in California, Australia, South Africa, and British Columbia. Before it has been refined, gold is almost always alloyed with silver; sometimes the proportion of silver is small, but occasionally it is very considerable. Usually, however, the proportion of gold ranges from 97 per cent. to about 87 per cent.

Gold is chiefly found in association with quartz. To extract it the rock is powdered and exposed, when wet, to mercury*, which dissolves the particles of gold. The amalgam thus obtained is distilled. The crushed ore may also be digested, after it has been roasted, with a solution of chlorine or bromine. It then yields a solution of gold chloride or bromide, which is mixed with ferrous sulphate to precipitate the precious metal.

A solution of cyanide of potassium is also used to extract the gold from the powdered rock. This salt appears to act only in the presence of air. The gold is liberated from the solution of the double cyanide electrolytically, or by the action of zinc.

The refining of gold, often called *parting*, may be effected by forcing chlorine gas through the molten metal; the chlorine combines with silver and copper, but leaves the gold unaffected. When the proportion of silver is large the metal may be granulated and boiled with oil of vitriol; the less valuable metal is converted into sulphate, which can be removed by means of water.

Pure gold, like pure silver, is too soft to resist ordinary wear and tear. It is hardened by adding copper or silver; the latter is still used by goldsmiths, but the standard alloy for British coinage consists of eleven parts of gold and one of copper. The density of such an alloy is 17.157, and that of gold itself 19.3. A new sovereign weighs 123.25 grains, and wears so well that it may be in circulation for eighteen years, under ordinary circumstances, before it loses

* Amalgamated copper plates are usually employed.

weight to the extent of one grain. When this occurs it is no longer legal tender.

The purity of gold is expressed by the number of carats of pure gold in 24 carats of alloy. Thus a sovereign is said to be made of 22 carat gold, that is, of an alloy containing 22 carats of gold in 24 carats. Its insolubility in nitric acid distinguishes gold from most other metals, and from alloys of similar colour.

The quality of gold may be judged, by an expert, by means of the 'touch-stone.' This is a piece of black basalt. When gold is rubbed upon its surface, it leaves a fine streak of metallic particles. If this is touched with strong nitric acid containing a trace of hydrochloric acid, the streak will remain unaffected if the gold is not below 18 carats fine. In the case of inferior alloys, the streak will give valuable indications of the quality of the gold if the effect of the nitric acid upon it is compared with its effect on the streaks made by a series of touch-neededles of known composition, which are kept for making such comparisons.

A more exact assay of gold is made by heating a weighed quantity of the metal with $2\frac{1}{2}$ times its weight of pure silver and 6 times its weight of pure lead on a tray, or cupel, made of compressed bone earth. When the cupel and its contents are heated suitably in a current of air, in a muffle furnace, the lead and copper are oxidized, and their oxides are absorbed by the cupel. When the remaining alloy of silver and gold 'brightens' (545) it is hammered flat, rolled into a thin coil, and boiled first with weak nitric acid and then with a stronger acid. This extracts the silver, leaving a little tube of gold, which is well washed, to remove every trace of silver nitrate, dried and weighed.

Pure gold is so malleable that a cube of it may be extended by hammering till its surface becomes 650,000 times as great as that which it originally possessed, and it may be drawn into very fine wire, but its malleability is reduced by the presence of other metals, and especially by an addition of lead or bismuth. When in very thin sheets it transmits light of a greenish-blue, violet, and finally of a red colour as its thickness diminishes. Objects made of inferior metals may be coated with gold by an electrical process analogous to that employed for electro-plating with silver.

556. Oxides of gold. Gold forms several oxides, viz. aurous oxide (Au_2O), auric oxide (Au_2O_3), and auroso-auric oxide (Au_4O_4). These are all decomposed by heat.

Auric oxide (Au_2O_3). Dissolve some gold in aqua regia; expel excess of acid by evaporating the solution, redissolve the residue in water, add excess of alkali, and pass sulphur dioxide into the solution. A brown precipitate of auric oxide will fall. It is easily decomposed by heat, and dissolves in alkalis, forming salts called aurates. Thus with potash the salt $\text{KAuO}_2, 3\text{H}_2\text{O}$ is formed.

557. Chlorides of gold. Gold combines with chlorine and bromine when cold or if moderately heated, but the compounds formed decompose if they are strongly heated.

Auric chloride (AuCl_3). This compound is formed by the direct combination of gold and chlorine. If a solution of gold in aqua regia be evaporated it deposits hydrated yellow crystals containing $\text{AuCl}_3, \text{HCl}$. Auric chloride is a red, crystalline, hygroscopic substance. It forms a series of double salts known as the chloroaurates; potassium chloroaurate ($2(\text{KCl}, \text{AuCl}_3), \text{H}_2\text{O}$) affords us an example of these salts. When auric chloride is heated it yields aurous chloride (AuCl) and finally gold.

Gold may be detected in solutions of its compounds by the brown precipitate of metallic gold which they form with ferrous salts. Also by the forming of a substance called 'purple of Cassius' when a mixture of stannous chloride and stannic chloride is added to a solution containing gold.

Compounds of gold are readily reduced before the blow-pipe; they yield beads or spangles of metallic gold which are insoluble in all acids except aqua regia.

PLATINUM (Pt): Atomic weight, 193.3.

558. Platinum is always met with in the metallic state. It is generally associated with iron, copper, osmium, iridium, rhodium and palladium, often also with gold. It is found in several parts of the earth, and the Ural Mountains have been a most important source of this metal.

Platinum may be extracted from the grains of native metal by treating them with nitric acid to remove copper, lead and silver, if these metals are present; washing the residue; digesting it with hydrochloric acid, to dissolve iron, and extracting what remains with aqua regia. The latter dissolves the platinum, rhodium, palladium and part of the iridium, and leaves an alloy containing osmium and some iridium. The platinum is then precipitated,

by adding ammonium chloride, as chloride of platinum and ammonium ($2\text{NH}_4\text{Cl}, \text{PtCl}_4$). The precipitate is well washed, and heated in a crucible till only spongy platinum remains. The platinum sponge may be welded into a mass by hammering it whilst hot, or it may be melted with an oxyhydrogen flame in a crucible made from a lump of quicklime or gas carbon. The product is not quite pure, but it can be used for most purposes.

Platinum is white, highly lustrous, very malleable and ductile, and, when pure, soft. Its density is 21.5. Its coefficient of expansion is almost the same as that of glass, and therefore a platinum wire can be sealed into a glass vessel without much risk of its breaking away from the glass on cooling. Its melting-point is about 1800° , and its power of occluding oxygen and hydrogen is so considerable, that if platinum black* be introduced into a mixture of the two gases they explode.

Like gold, platinum does not readily enter into combination; it is hardly attacked by any single acid, though it dissolves in aqua regia, and combines with chlorine. Both the chlorides and the oxides of platinum are decomposed by heat.

Platinum is chiefly useful on account of its high melting-point, and its indifference to acids. But it is attacked by caustic alkalis, and readily forms fusible alloys with lead and many other metals. An alloy containing iridium, rhodium, and platinum is harder than pure platinum, and even more difficult to corrode, and is largely used as a substitute for platinum.

559. Oxides of platinum. **Platinic oxide** (PtO_2). Dissolve some platinum in aqua regia, add excess of solution of soda, boil and add acetic acid. Hydrated platinic oxide will be precipitated. This is resolved into water and platinic oxide (PtO_2), if it is moderately heated: but if it is strongly heated the platinic oxide is decomposed. It is soluble both in acids and alkalis.

Platinous oxide (PtO). This is a black powder which may be prepared by heating the hydroxide formed by the action of potash on platinous chloride. It is soluble in acids and in alkalis, and is reduced to the metallic state when strongly heated.

560. Platinic chloride (PtCl_4). This compound may be obtained by dissolving metallic platinum in aqua regia. If the solution be evaporated on a water bath it yields crystals having the composition

* A very finely divided form of platinum.

$\text{PtCl}_4 \cdot 2\text{HCl} \cdot 6\text{H}_2\text{O}$ or $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. Platinic chloride forms double salts with the chlorides of the alkali metals and with chloride of ammonium. Potassium chloroplatinate (K_2PtCl_6) forms as a yellow crystalline precipitate, when a solution containing potassium chloride is mixed with solution of platinic chloride. Sodium chloroplatinate is very soluble, but the ammonium salt cannot be distinguished easily from potassium chloroplatinate, and is obtained in a similar manner. The former is decomposed when it is strongly heated, and leaves a residue of platinum; the latter evolves chlorine, leaving a mixture of potassium chloride and metallic platinum.

Anhydrous platinic chloride may be prepared by heating chloroplatinic acid ($\text{PtCl}_4 \cdot 2\text{HCl} \cdot 6\text{H}_2\text{O}$) to about 165° in a current of dried hydrochloric acid.

If platinic chloride be heated to about 200° in a current of dried hydrogen chloride until no more chlorine is evolved, it leaves a dark-greenish residue of platinous chloride. Platinous chloride is insoluble in water, and is decomposed when strongly heated. Like platinic chloride it forms double salts with the chlorides of potassium and ammonium.

Two sulphides of platinum are known. They are produced by the action of hydrogen sulphide on the chlorides. The disulphide (PtS_2), like auric sulphide, dissolves in solutions of alkaline sulphides.

If we look once more at the table on p. 181, we shall see that the various series in the eighth group are not represented by single elements but by groups of elements, which do not differ greatly in their atomic weights.

It is doubtful whether copper, silver, and gold do not properly belong to Group I, and it will be a useful exercise for the student to endeavour to decide whether these elements should be placed in the first or in the eighth group

CHAPTER XXXVI

RADIO-ACTIVE SUBSTANCES—RADIUM, POLONIUM, ACTINIUM,
URANIUM, THORIUM.

561. Radio-activity. In 1896 Monsieur H. Becquerel discovered, partly by accident, that if crystals of the sulphate of uranium and potassium are laid above a sensitive photographic plate wrapped in black paper and placed in the dark, they so act on the plate that a black image, or silhouette, is obtained when the plate is developed. He found that this was no temporary property of the salt, but highly persistent, and that it was shared by other uranium salts and also by the metal uranium. The radiations which are the cause of this phenomenon are known as Becquerel Rays, and they resemble the Röntgen or X Rays in many respects. Thus in their presence air becomes a conductor of electricity; and damp, dust free air deposits fog. They will pass through layers of such substances as paraffin, quartz, Iceland spar, sulphur and thin sheets of metal even more freely than the X Rays, and they cannot be reflected, refracted, nor polarized like ordinary light. Substances which emit radiations such as these are said to be 'Radio-active.' It is not possible to discuss and describe all the known radio-active substances here, but it may be said that radio-activity is not only exhibited by uranium and its salts, a good many other substances exhibit the phenomenon, though usually in a far smaller degree.

Becquerel's observation proved highly prolific. Very soon Madame Sklodowska Curie and Dr. Schmidt followed it up by discovering, independently, that thorium compounds also are radio-active—a fact which can easily be verified, as also can the original observation of M. Becquerel, by any one who is familiar with the operations of photography.

This last discovery was soon followed by the observation, by Madame Curie in 1898, that the radio-activity of a sample of pitchblende, an ore containing uranium, was distinctly greater than the uranium it contained would account for. This led Madame and Monsieur Curie to analyse a large quantity of the mineral in question, and to measure the radio-active power of each of its constituents, with the result that they presently discovered two new substances.

First polonium, which was found associated with bismuth. And secondly, radium, which was found in association with the barium which this mineral contains.

Thorium and its compounds are also radio-active, and a fourth substance, actinium, has been discovered by M. Debierne and by Dr. Giesel.

Neither polonium nor actinium have as yet been isolated in the form of a salt, and some doubt still remains as to the nature of the former. Radium salts, on the other hand, have been prepared, thus we know more about this latter substance than about either polonium or actinium, and, therefore, I shall confine my further remarks to the properties of radium and its compounds.

Radium, if it be a divalent element, has the atomic weight 225, or possibly 258. It occurs chiefly, as I have already explained, in pitchblende, but it can be extracted, even from pitchblende, only to the extent of a few decigrams from a ton of the raw material. It has also been found in a few other minerals, has been detected in the Bath waters and elsewhere, and probably will be found to be more widely distributed. A ton of the residue left after the uranium has been extracted from pitchblende may yield 10 to 20 kilograms of a mixture of the insoluble sulphates of barium, lead, iron and calcium. This mixture contains most of the radium. To extract the latter it is treated with a hot solution of sodium carbonate, and the carbonates thus formed are converted into chlorides by dissolving them in a solution of hydrochloric acid. The lead and iron are precipitated from this solution by hydrogen sulphide and ammonia respectively, and afterwards the barium, calcium and radium are reprecipitated as carbonate, converted again into chloride and washed with strong hydrochloric acid to remove the calcium salt. The barium-radium chloride thus obtained, which contains only a trace of radium, is dissolved in hot water and allowed to crystallize. When part of the salt is deposited, the crystals are separated from the mother liquor. The crystals contain most radium, the mother liquor less. The latter is evaporated to dryness, and the crystals and the residue from the mother liquor are then separately re-dissolved and fractionally crystallized in a similar manner. By repeating these fractional crystallizations systematically products 5,000, 50,000 and 300,000 times as active as uranium may be obtained.

The purest radium chloride is said to be colourless when first made; that which still contains a little barium chloride has a yellow or

orange tinge. The barium salt may be got rid of by adding alcohol to a solution of the mixed chlorides, and hydrochloric acid of gradually increasing strength may be substituted for water with advantage in the later stages of the fractionating process.

The salts of radium, so far as they are known, resemble those of barium in their properties, except that the former gradually become coloured. They are luminous in the dark, exhibit a definite spectrum, and continuously evolve heat. It is calculated that one atomic proportion in grams, 225 grams, of radium would evolve about 22,500 calories per hour, and that some thousands of years would pass before its powers would be exhausted. The radio-active power of a radium salt is destroyed by strong heat, but only for a time. A freshly prepared solution is very active, but its power rapidly falls off if it is exposed to the air. It is impossible to say how much radium, in the form of its salts, has been prepared—probably only a very few grams.

When radium was first discovered its radiations were thought to be similar to Röntgen rays. Then 'electrons' were detected, and afterwards heavier particles carrying positive charges of electricity. Subsequently Professor Rutherford showed that its radio-activity is accompanied by a change, which seems to be a disintegration, in the course of which new substances are formed, and still more lately helium has been discovered as a product of this change by Sir William Ramsay and Mr. Soddy.

562. *The radiations of radium.* These have been divided into the α , β , and γ Rays. The last closely resemble Röntgen Rays. They are unaffected by magnetic fields and are intensely penetrative, passing through sheets of lead of considerable thickness, and these rays alone of the radium rays can penetrate the eyelids so that they can be identified by the sense of diffused light which one perceives when a few milligrams of a radium salt are held near the closed eye in a dark room in the evening. They can also be distinguished by placing the radium salt in a leaden box 1 c.m. in thickness and observing its power to excite luminosity on a piece of the mineral willemite.

One of the great achievements in physics during the latter part of the nineteenth century was the discovery, by Professor J. J. Thomson and his colleagues, in the cathode stream of the Crookes' vacuum tube, of particles so small that about 700 of them would be required to produce a mass equal to that of an atom of hydrogen. These particles carry negative charges of electricity, and are deflected by

electric and magnetic fields; they pass through thin sheets of metal, cause damp, dust-free air to form mist, and render air a conductor of electricity. They move with a velocity equal to one-tenth that of light. They are often called 'electrons*.' Now the β Rays of radium exhibit the same properties as electrons, but they move much more quickly than the electrons in the cathode stream, and are more penetrating. Hence the β Rays are considered to be 'electrons.'

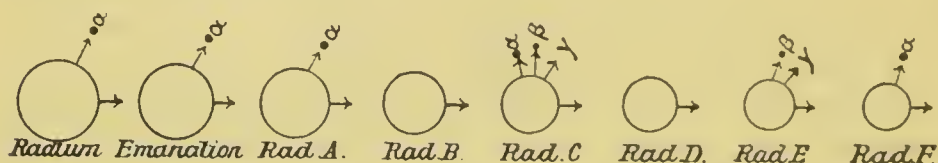
The α Rays were the last discovered. These are far heavier than the β rays, and are very easily stopped. Sir William Crookes has succeeded in deflecting them by powerful magnets, and the deflection, which is the opposite sense to that of the cathode stream, shows they carry positive charges. Sir William Crookes has also shown us how to recognize the α rays by letting them strike screens covered with phosphorescent zinc sulphide, as in the spinthariscopes. The greater part of the energy of radium emitted in the form of ionizing radiations is due to these last rays.

Such substances as diamond, willemite, barium platino-cyanide, &c., become phosphorescent if the rays of radium fall upon them much as they do under the influence of cathode rays, the effects produced being often exceedingly beautiful.

563. *The emanation of radium.* If radium be heated strongly, or if it be dissolved in water, something is given off which mixes with gases, and has, in general, the properties of a gas. This has been known as the emanation of radium, and it has been shown by Rutherford and Soddy that the radio-activity of radium, thorium, and actinium is accompanied by the formation of series of new substances which exhibit distinct physical and chemical qualities, and may be identified by the rates at which their respective radio-activities diminish. Radium, for example, produces 'radium emanation,' a chemically inert gas which condenses at about $-150^{\circ}\text{C}.$, loses half its activity in four days, and is thus easily distinguished from the parent radium, since the latter is a solid and disintegrates so slowly that no less than thirteen hundred years would elapse before its radio-activity would be diminished to an equal extent. Radium emanation in its turn gives rise successively to six new products. First we get radium A, B, and C. These differ in volatility, the first loses half its activity in three minutes; whilst the second and third only undergo

* This term was originally applied to the charge of electricity carried by an atom of hydrogen in electrolysis. Hence the term 'corpuscle' is proposed for the particles in the cathode stream by some authorities.

corresponding changes in twenty-eight and twenty-one minutes respectively. From radium C springs radium D, which gives off no rays and retains half its powers at the end of the comparatively long period of forty years. This generates radium E, whose period is six days; and finally from radium E we get radium F, which probably is polonium, and has a period of 143 days. Most of these changes are accompanied by characteristic radiations as shown in the diagram given below, which is similar to that introduced by Dr. Rutherford into his Bakerian Lecture:—



Radium and the products of its disintegration.

If we accept this explanation of the peculiar properties of radium and continue to regard that substance as an element, then it seems clear that we must definitely abandon the idea that the atoms of Dalton are as simple in their constitution as Dalton and his successors have supposed them to be. On the other hand, the facts as interpreted by Professor Rutherford must surely make us doubt whether these radio-active substances really are elementary in their nature. It will be seen from the diagram that most of the substances mentioned above give off one or more α particles in the course of its disintegration. These may very well be supposed to be atoms of helium, first, because the masses of these particles and those of the helium atoms correspond fairly well, and secondly, because helium has been shown to be a product of the disintegration of radium*. There is, however, nothing to justify the assumption that helium is the final product of the disintegration of radium, and Professor Rutherford is disposed to hold that the expulsion of the α (or helium?) particles, as far as they have been traced, finally leaves behind them a much heavier particle than an atom of helium. In which case it would seem that the so-called radio-active elements must be regarded as compounds of helium with some other substance or substances not yet identified.

The emanation of radium, which behaves like a gas, may be driven from radium by heat. It is given off when a salt of radium is dissolved

* See *Phil. Trans.*, 1904.

in water, and its removal deprives the radium for the time being of 70 per cent. of its heating power. Its energy is so great that if a cubic centimetre of the emanation of radium could be collected in one place it is thought probable it would fuse the containing vessel. After being heated radium recovers its original activity in about a month.

564. The discovery of radium and its unique properties raises some important questions. Whence, for example, does this remarkable substance derive its vast supplies of energy? It has been suggested by some that radium may act as a transformer, picking up energy in some way from its environment and giving it out again as light, heat, &c., during the disintegrations discussed above. Another school, and this perhaps predominates at present, regards radium as a form of matter endowed at its origin with relatively vast stores of energy which is subsequently liberated in the changes which the radium continuously undergoes; and it has been suggested, originally perhaps in order to compose certain outstanding differences between the geologists and physicists on the subject of the age of the sun, that the heat and light given out by the sun would be accounted for by the presence in it of no more than three or four grams of radium in each cubic metre of its substance. But except such evidence as the presence of helium in the sun may afford, we have not much, I think, to support the hypothesis that the sun's heat may be due largely to radium.

565. *The origin of radium.* Rutherford finds that the half of any given quantity of radium would be transformed after about 800 years, and that after so comparatively brief a time as 16,000 years only $1/10^6$ of this radium would remain unchanged. Thus, if the whole earth had been composed of radium 16,000 years ago its activity to-day would not be greater than that of pitchblende. Hence, since radio-active minerals are doubtless very much older than this, we may conclude that the supply of radium in these minerals is maintained by some process which continuously produces this substance from some other constituent of the mineral. Now radium and uranium nearly always occur together; the amount of radium in a mineral being, it is said, proportional to the amount of uranium; uranium has an average life, 5×10^8 years, far greater than that of radium; the activity of pitchblende is about what might be expected if uranium were the parent of radium and, finally, though the matter is hardly beyond dispute at present, trustworthy observers believe they have detected the production of minute traces of radium from the more familiar element.

APPENDIX

I. THE BALANCE.

A BALANCE, such as that which is shown in Fig. 142, provided with agate knife edges and planes, capable of carrying 100 grams, and

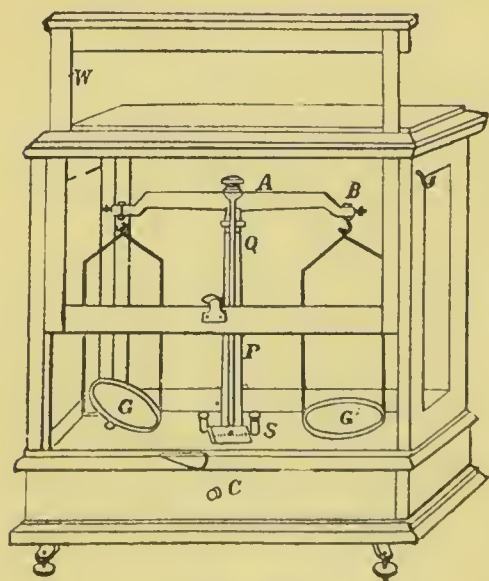


Fig. 142.

sensitive to 0.5 milligram, can be purchased for £3 or less, and a similar balance, to carry 250 grams, and sensitive to 1 milligram, can be obtained for about ten shillings more. It consists of a beam *A*, carrying agate knife edges at *B*, from which the pans *G G'* are suspended upon agate planes. The beam *A* is supported by agate knife edges on agate planes on the top of the pillar *P*, and the parts of the balance are so arranged that when it is out of use the knife edges no longer rest on the planes. A pointer *Q*, attached at right angles to *A*, swings

before a scale *S*, and enables the observer to study the oscillations of the beam. At each end of the beam are small movable weights which run on screws. These enable one to bring the two sides of the balance into equilibrium, when it is necessary to do so.

Before using a balance the student should verify the above statements by carefully taking the instrument to pieces and putting it together again. At any rate this should be done before every student by a teacher.

Use of the balance. Close the window W to prevent draughts, turn the handle C , and watch the oscillations of the pointer. If it swing to equal distances on each side of the central line of the scale, the balance is duly adjusted. If it does not do so, adjust the position of one of the little weights at the ends of the beam till the pointer does oscillate equally about the centre of the scale.

Now place some object of known weight, say a penny*, on G , place a weight on G' , and put the balance in action. If the weight be greater than the penny, replace it by the weight next in size; if this be too great, repeat the process until the weight on G' is less than the penny. Then add the weight next in order, and if the two weights be too little, add the next, and so continue, removing or adding the weights in order, until the penny and the weights exactly balance each other.

Reading the weights. In an ordinary box of weights, the weight marked 100 weighs 100 grams.

That marked 50 weighs 50 grams					
„	„	20	„	20	„
„	„	10	„	10	„
„	„	5	„	5	„
„	„	2	„	2	„
„	„	1	„	1	„
„	„	.5	„	$\frac{5}{10}$	of a gram
„	„	.2	„	$\frac{2}{10}$	„
„	„	.1	„	$\frac{1}{10}$	„

Similarly, that marked .05 is $\frac{5}{100}$ of a gram, and so with the others. Hence, if the weights marked 50, 20, 5, .5, .1, and .05 are required to balance an object, its weight is 75 grams + $\frac{6}{10}$ + $\frac{5}{100}$ of a gram, which is written 75.65 grams.

Sometimes the figures on the smaller weights give their weights as milligrams; then we have 500 instead of .5, 200 instead of .2.

Before attempting work which depends on the use of the balance, the student should practise weighing, using objects of known weight given to him by his instructor, until he can weigh correctly.

The following precautions must always be taken:—

1. Take your weighings with the balance case closed to prevent draughts of air from causing errors.

* The teacher should supply this.

2. Assure yourself that the pans of the balance are clean, and that the instrument is in equilibrium before you use it.

3. Never weigh anything whilst it is hotter or colder than the air.

To learn the reason for this last precaution, weigh a penny, then warm it, leaving the weights in the pan, replace the penny on the scale-pan whilst it is still warm, again set the balance in action and observe the result of your experiment.

II. SPECIFIC GRAVITY AND STRENGTH OF ACIDS AND OF AMMONIA.

The tables which follow give, as will be seen, curves to enable the student to find the strength of an acid (p. 96), when he has ascertained its specific gravity. As none of these acids occur in the pure state in commerce, the curves will be found useful when the work to be done demands the use of a fixed weight of an acid or of ammonia.

Suppose, for example, that the student wants 10 grams of real HCl, and that the acid in the laboratory has the density 1.1 :—

From Curve I he finds that acid of this density contains 20% of HCl. Then since 20 grams of HCl are in 100 grams of this solution,

10 " " 50 " "

And he may take 50 grams, or $\frac{50}{1.1}$ c.c., of the solution having the density 1.1 for his work.

PROBLEMS

Answers will be found on p. 513.

A Table of Atomic Weights will be found on page 47.



SECTION I.

1. Find the molecular weights of mercury oxide (HgO), silver oxide (Ag_2O), potassium chlorate (KClO_3), sulphuric acid (H_2SO_4).

2. Calculate the weights represented by:— 2ZnSO_4 ; $3\text{P}_4\text{O}_{10}$; $2\text{H}_2\text{O}$; $2(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$; $\frac{1}{2}(\text{HNO}_3)$; 2NaCl ; KClO_4 ; Fe_2O_3 ; CuO .

3. Iron rust has the formula Fe_2O_3 . How much iron (Fe) is there in 10 grams of it?

4. Water has the formula H_2O . How much hydrogen and oxygen are there in 100 parts of it?

5. Find how much a molecule of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) weighs.

6. How much carbon is there in 1 kilo. of sugar?

7. Find the molecular weight of spirit of wine ($\text{C}_2\text{H}_6\text{O}$).

8. How much hydrogen is there in 100 grams of spirit of wine?

9. Find the percentage composition of spirit of wine.

10. Find how much potassium chloride (KCl) will be formed if 64 grams of oxygen are made from the chlorate (KClO_3).

11. Find the percentage composition of potassium chlorate.

12. Find how much heavier a molecule of oxygen (O_2) is than a molecule of hydrogen (H_2).

13. How much water can you get by reducing 25 grams of oxide of copper with hydrogen?



14. Find the percentage of hydrogen in marsh gas (CH_4).

15. How much carbon is required to reduce 165 grams of carbon dioxide (CO_2) to carbon monoxide (CO)?



16. How much sulphur is there in 268.3 grams of zinc sulphate?

17. How much zinc and sulphuric acid respectively must be used to prepare 36 grams of hydrogen?

18. How much metallic chloride will be formed by the direct combination of 85 grams of mercury (Hg) with chlorine? The product is HgCl_2 .

19. What quantity of chlorine will take the place of 40 grams of bromine in potassium bromide?



20. How much *air* will be required to burn 150 grams of sulphur if SO_2 is produced?

21. A compound of iron and oxygen contains—

Iron	.	.	.	.	.	77.8
Oxygen	.	.	.	.	.	22.2
						100.0

Find its formula.

22. A sugar contains—

Carbon	.	.	.	.	.	40.0
Hydrogen	.	.	.	.	.	6.7
Oxygen	.	.	.	.	.	53.3
						100.0

Find its simplest formula.

23. An acid contains—

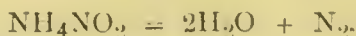
Carbon	.	.	.	.	.	32
Hydrogen	.	.	.	.	.	4
Oxygen	.	.	.	.	.	64
						100

Find its simplest formula.

24. How many litres of hydrogen are obtained by dissolving 96 grams of magnesium in sulphuric acid?

25. If 10 grams of water are decomposed, what volumes of hydrogen and oxygen will be obtained?

26. What volume of nitrogen can be got from 10 grams of ammonium nitrite?



27. What volume of hydrogen chloride will be formed if 5 grams of silver chloride are heated in hydrogen?

SECTION II.

Finding formulae (p. 114).

28. Hydrogen was passed over copper oxide with the following results:—

Weight of CuO and tube	=	334.598	grams.
„ Cu and tube	=	314.236	„
„ drying tubes	=	426.358	„
„ „ and water formed	=	449.263	„

Calculate the percentage composition and formula for water from these data.

29. Find the formula for the substance having the following composition :—

Fe = 20.15 per cent.

S = 11.51 „

O = 23.02 „

(H₂O) = 45.31 „

30. Find the formula of the following substance on the assumption that each molecule contains 12 atoms of carbon :—

Carbon = 42.11 per cent.

Hydrogen = 6.43 „

Oxygen.

31. A silver salt contains—

Silver 64.68 per cent.

Carbon 14.37 „

Hydrogen 1.79 „

Find the simplest formula of the acid of this salt (N.B. Ag. Atomic weight 107).

Equivalent weights (p. 99) and atomic weights (p. 107).

32. When hydrogen was passed over excess of oxide of copper, the oxide lost 59.789 grams and 67.282 grams of water were formed. Calculate the equivalent weight of oxygen, assuming that of hydrogen to be 1.

33. If 88.88 parts of oxygen unite with 11.11 parts of hydrogen, and if the equivalent of oxygen be 100, what is the equivalent of hydrogen?

34. 0.5 gram of zinc when dissolved in acid gives 183 c.c. of hydrogen at 9° and 748 mm. Find the equivalent of zinc.

35. 1.586 parts of iron give 2.265 parts of oxide; the formula of the latter substance is Fe₂O₃. Calculate the atomic weight of iron corresponding to these data.

36. 10 grams of platinum give 24.735 grams of a compound, having the formula K₂PtCl₆. Find the atomic weight of platinum corresponding to these data.

37. One gram of a certain metal when dissolved in hydrochloric acid evolves 1242 c.c. of hydrogen at normal temperature and pressure. The specific heat of the metal is 0.23. Find its equivalent weight, its atomic weight, and its valency.

38. In water and ammonia hydrogen combines with oxygen and with nitrogen in the proportions 1 : 8 and 1 : 4 $\frac{2}{3}$ by weight. Explain why it is that 8 and 4 $\frac{2}{3}$ are not taken for the atomic weights of oxygen and nitrogen, but that these respective numbers are multiplied by 2 and 3 to obtain their atomic weights.

39. Calculate the equivalent of copper if 73.34 grams of the metal combine with oxygen to form 91.79 grams of copper oxide.

40. The specific heat of an element is 0.198. What is its probable approximate atomic weight?

41. What is the probable specific heat of barium?

Diffusion (p. 170).

42. If 16 c.c. of hydrogen diffuse in 100 seconds, what volume of sulphur dioxide (SO_2) will diffuse in the same time under equal conditions?

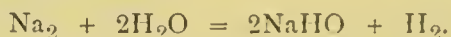
43. If 374.2 c.c. of hydrogen diffuse through a crack in 10 seconds, how much ethene (C_2H_4) will diffuse in the same time?

Problems involving corrections for temperature and pressure (pp. 74, 75).

44. If 72 grams of mercuric oxide are heated, what volume of oxygen at 91° and 380 mm. will be given off?

45. What mass of oxygen would occupy 78 litres at 12° , and how much KClO_3 must be heated to make it?

46. 1000 c.c. of hydrogen at 17° and 800 mm. are required. How much sodium must be thrown into water?



47. How many litres of hydrogen at 10° and 385 mm. will you obtain by passing 2 grams of steam over red-hot iron?

48. How much zinc is required to obtain 100 litres of hydrogen at 91° and 720 mm.?

49. What volume of oxygen at -140° and under a pressure equal to 215.2 metres of mercury could be made from 613 grams of potassium chlorate?

50. What do 100 litres of nitrogen weigh?

Problems on atomic weights, molecular weights, &c.

51. The atomic weight of lead is 206.5 ($0 = 16$), and it is found that 13.67 grams of a certain compound contain 12.69 grams of lead and 0.98 gram of oxygen. Find a formula for the compound.

52. Prove the formula $M = 2d$, where M is the molecular weight and d the density of a gas referred to hydrogen.

53. 0.119 grams of a liquid yield 22.8 c.c. of vapour. Find its density and molecular weight.

54. The specific heat of a metal is 0.281; 0.125 of its chloride contains 0.054 of metal. Calculate its exact atomic weight.

55. A silver salt of a monobasic acid contains 63.53 per cent. of silver. Find the molecular weight of the acid.

56. 1.45 grams of pure carbon give 5.302 grams of carbon dioxide. Carbon dioxide is about 22 times as heavy as hydrogen. The atomic weight of oxygen is 15.9. Find the exact molecular weight of carbon dioxide from these data.

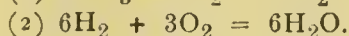
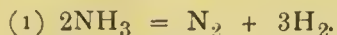
57. Aluminium chloride contains 79.0 per cent. Cl and 21.0 per cent. Al. Its vapour density is about 132. The specific heat of aluminium is 0.225. Find its exact atomic weight.

Miscellaneous problems.

58. Some barium dioxide is treated with carbon dioxide and water (1). The product is then boiled (2). How much oxygen will be produced if 19.6 grams of barium carbonate are formed?



59. 29 c.c. of ammonia are decomposed by electric sparks (1); the product is exploded with 30 c.c. of oxygen (2). What volume of what gases will remain?



60. Ordinary nitric acid ($D = 1.4$) contains 65 per cent. of HNO_3 . How much of it must we use to make 1 litre of acid containing 0.63 gram of real acid per c.c.?

61. On adding argentic nitrate to a given quantity of sea-water a precipitate of 20 grams of argentic chloride is thrown down. What weight of combined chlorine is present?

Silver = 108. Nitrogen = 14. Oxygen = 16. Chlorine = 35.5.

62. What weight of calcic carbonate must be decomposed by hydrochloric acid to yield sufficient carbon dioxide to convert 50 grams of sodic hydrate into sodic carbonate?

(Ca = 40. C = 12. O = 16. Na = 23.)

63. One gram of soda-ash acted on by sulphuric acid yields 150 c.c. of carbon dioxide at standard temperature and pressure. What percentage of anhydrous sodic carbonate was present?

(Sodium = 23. Carbon = 12. Oxygen = 16.)

64. Find how many grams of calcium carbonate are needed to give 56 c.c. of carbon dioxide when treated with acid. (Ca = 40.)

65. What compound is formed when potassium acts upon water? If 10 grams of potassium are placed on 100 grams of water, what weight of the compound will be formed and what weight of water left unacted upon?

(Potassium = 39. Oxygen = 16.)

66. Calculate the weight of zinc which would be necessary to generate sufficient hydrogen to fill a gasometer which holds 120 litres at 15° and 730 mm. pressure.

Given:— Zn = 65. H = 1. 1 litre of H weighs 0.09 gram at 0° and 760 mm.

67. 12 grams of calcium carbonate were added to 120 grams of a solution of hydrochloric acid. After all action had ceased 2.5 grams were left undissolved. What was the strength of the acid?

(Ca = 40. H = 1. O = 16. C = 12. Cl = 35.5.)

68. 12 grams of carbon are ignited in an excess of carbonic acid gas: what weight of carbonic oxide is produced? What volume would this carbonic oxide occupy at 91° and 380 mm. pressure?

69. What volume of nitric oxide (at 0° and 760 mm.) can be produced from one gram of nitric acid by the action of copper?

(N = 14. O = 16.)

70. Calculate the smallest number of cubic centimetres of atmospheric air which must be mixed with (a) 60 c.c. of carbon monoxide, (b) 60 c.c. of marsh gas (methane), in order that there may be no unburnt carbon monoxide in the first case, and no unburnt marsh gas in the second, when the mixtures have been set on fire.

71. If one grain of hydrogen at normal pressure and temperature fills 11,200 c.c., what weight of iron must be dissolved in acid to procure a cubic metre of hydrogen? ($\text{Fe} = 56$.)

72. In order to find the strength of a sample of hydrochloric acid, 10 grams of it were taken, and after dilution a piece of marble weighing 7 grams was placed in it; after all action had ceased 2.2 grams of marble were left undissolved. Calculate the percentage strength of the acid.

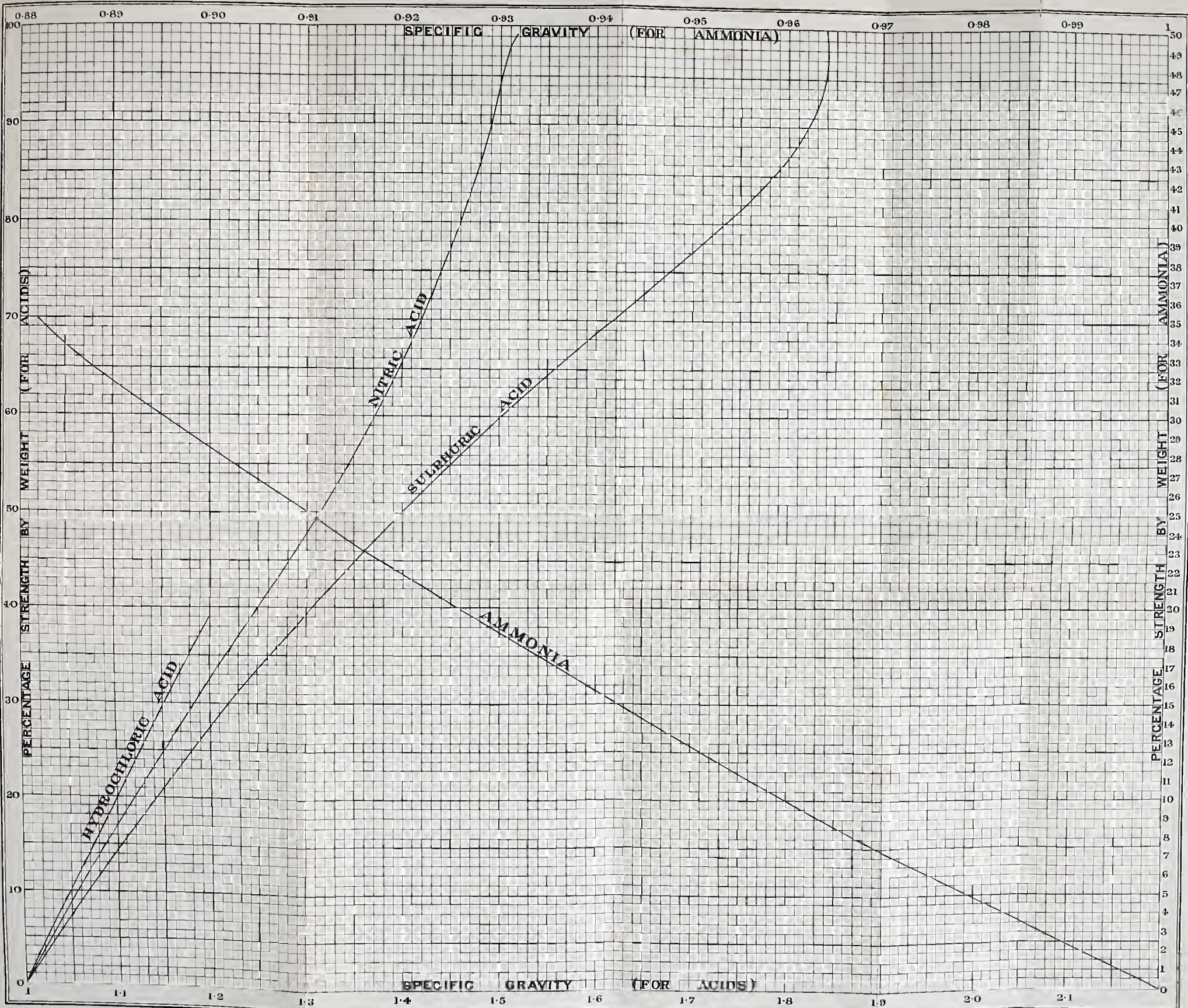
73. Calculate the volumes of carbon dioxide and sulphur dioxide produced by the complete combustion of 10 grams of carbon disulphide. If 100 litres of air be taken in which to perform the combustion, calculate the respective volumes of the resulting gases.

(Air = 21 vols. oxygen + 79 vols. nitrogen.)

74. Find the number of grams of H_2SO_4 in a litre of a sample of sulphuric acid, if 10 c.c. of it neutralize 2.92 grams of pure sodium carbonate, and if the same volume liberates 612 c.c. of hydrogen by its action on zinc. Compare the two results.

75. 130 vols. of marsh gas and carbon monoxide were mixed with 400 vols. of oxygen and exploded. After combustion 390 vols. remained; after absorption of the carbon dioxide 260 vols. were left. Required the percentage composition of the original gas.

76. A mixture of marsh gas and olefiant gas, occupying 6.3 c.c., requires for its complete combustion 15.4 c.c. of oxygen and produces 9.1 c.c. of carbon dioxide. Find the volume of each gas.



SOLUBILITY CURVES FOR ACIDS AND AMMONIA.



INDEX

The figures in **heavy type** refer to the numbered sections, the others to pages.

Absolute temperature, 76, 65.

Absorption spectra, 382, 336.

Acetylene, 345, 302.

Acid:—

acetic, 342 *d*, 299.

antimonic, 443, 463.

arsenic, 305, 270.

boric, 359, 318.

bromic, 209, 162.

chloric, 202, 152.

citric, 342 *g*, 299.

cyanic, 330, 289.

cyanuric, 330, 289.

fluosilicic, 222, 175.

gallic, 342 *h*, 299.

hydrazoic, 267, 223.

hydriodic, 214, 166.

hydrobromic, 206, 157.

hydrochloric, 191, 141.

hydrocyanic, 327, 286.

hydrofluoric, 219, 171.

hypochlorous, 199, 148.

hypiodous, 216, 168.

hypophosphorous, 301, 264.

hyposulphurous, 248, 203.

iodic, 217, 169.

malic, 342 *g*, 299.

metaphosphoric, 299, 261.

metastannic, 436, 443.

muriatic, 191, 141.

nitric, 269, 225.

nitrous, 275, 236.

Nordhausen sulphuric, 238, 193.

oleic, 338, 295.

orthophosphoric, 294, 258.

oxalic, 342 *e*, 299.

oxalic, normal, 147, 116

palmitic, 340, 295.

perchloric, 203, 153.

perchromic, 451, 485.

periodic, 218, 169.

permanganic, 467, 516.

persulphuric, 248, 204.

phosphoric, 294, 258.

phosphorous, 300, 263.

prussic, 327, 286.

pyrophosphoric, 298, 260

silicic, 354, 308.

stannic, 436, 442.

stearic, 338, 295.

sulphuric, 238, 192.

— fuming, 238, 193.

sulphurous, 235, 187 ; 236, 189.

tannic, 342 *h*, 299.

tartaric, 342 *f*, 299.

thiocyanic, 331, 289.

thiosulphuric, 249, 205.

Acidimetry, 144, 116.

Acids and metals, 129, 109.

— basicity of, 136, 114.

— definition of, 134, 111.

— densities of, 498.

— hydrogen theory of, 133, 111.

— oxygen theory of, 131, 110.

— salts from, 94 *c*.

— strength of, 150, 116 ; 498.

— standard, 153 *g*.

— thionic, 251, 206.

Actinium, 490, 561.

Affinity, 360, 319.

— constants, 362, 320.

Air, absorption of, by burning substance, 3, 4.

— analysis of, 72, 62.

— components of, 81, 68.

— composition by weight, 79, 66.

— constitution of, 81, 68.

— dissolved in water, 7, 7.

— impurities in, 83, 69.

— not a compound, 79, 67.

- Alcohol, 342, 296.
 Aleoholic fermentation, 342 *a*, 297.
 Alkalimetry, 144, 116.
 Alkalis, salts from, 94 *e*.
 — strength of, 150, 116.
 Allotropy, 162, 124.
 Alums, 430, 431.
 Alumina, 429, 429.
 Aluminium, 428, 428.
 — chloride, 429, 430.
 — silicate, 430, 432.
 — sulphate, 430, 431.
 Amalgams, 423, 415.
 Ammonia, 259, 217.
 — soda process, 402, 357.
 Ammonium, 408, 371.
 — carbonates, 409, 375.
 — chloride, 408, 372.
 — hydrosulphide, 409, 376.
 — metallic derivatives of, 409, 378.
 — nitrate, 408, 373.
 — phosphates, 409, 377.
 Amygdalin, 328, 286.
 Analysis, 49, 44.
 — volumetric, 144, 116.
 Animal, life processes of, 93, 78.
 Antimonous oxide, 443, 461.
 Antimony, 442, 459.
 — hydride, 443, 460.
 — pentaehloride, 444, 465.
 — pentoxide, 443, 463.
 — sulphides, 444, 466.
 — tetroxide, 443, 462.
 — trichloride, 444, 464.
 Apatite, 286, 248.
 Appendix, 496 and 498.
 Aqua fortis, 269, 225.
 — regia, 280, 242.
 Argentic ehloride, 483, 548.
 — iodide, 483, 552.
 — nitrate, 483, 549.
 — oxide, 482, 547.
 — phosphate, 483, 551.
 — sulphate, 483, 550.
 — sulphide, 483, 553.
 Argon, 259, 218.
 Arsenic, 302, 267.
 — anhydride, 305, 270.
 — halides, 306, 272.
 — oxide, 305, 270.
 — sulphides, 306, 271.
 — trihydride, 303, 268.
 Arsenious oxide, 304, 269.
 Arsenites, 304, 269.
 Arsine, 303, 268.
 Atmosphere and plants, 91, 77.
 Atomic theory, 101, 88.
 — weights, 107, 94.
 — — table of, 47.
 Atoms, 101, 88.
 Available ehlorine, 250, 205.
 Avogadro's hypothesis, 103, 91.
 Azoimide, 267, 223.
 Balance, 496.
 Baking powder, 342 *g*, 299.
 — soda, 342 *g*, 299.
 Barium, 415, 395.
 — carbonate, 416, 398.
 — dioxide, 155, 117.
 — monoxide, 415, 396.
 — sulphate, 416, 397.
 Bases, 134, 112.
 Beer, 342 *b*, 298.
 Beryllium, 417, 399.
 Bessemer process, 457, 492.
 Bicarbonates, 318, 281.
 Bismuth, 445, 468.
 — nitrate, 446, 472.
 — pentoxide, 446, 470.
 — sulphide, 446, 473.
 — trichloride, 446, 471.
 — trioxide, 445, 469.
 Black-ash process, 400, 357.
 Blast furnace, 453, 489.
 Bleaching, 187, 140; 235, 181.
 — powder, 199, 150.
 — liquid, 199, 150.
 Boiling-points, determination of, 16, 15.
 — influence of pressure on, 20, 21.
 Bone black, 311, 275.
 Borax, 359, 318.
 Boron, 358, 317.
 Bread, 342 *d*, 298.
 Brimstone, 225, 178.
 Brin's process, 155, 117.
 Bromates, 209, 162.
 Bromides, metallic, 208, 158.
 Bromine, 204, 156.
 — chloride of, 209, 160.
 — oxyacids of, 209, 161.
 Bunsen burner, 89, 75.
 Burette, calibration of, 144, 116.
 Butter, 342, 295.
 Cadmium, 422, 414.
 Cæsium, 407, 370.
 Calcium, 410, 379.

- Calcium carbide, 414, 387.
 — carbonate, 413, 384.
 — chloride, 138, 115 ; 412, 383.
 — dioxide, 412, 381.
 — fluoride, 412, 382.
 — hydroxide, 412, 381.
 — oxide, 410, 380.
 — phosphates, 413, 386.
 — sulphate, 413, 385.
 — sulphides, 414, 387.
 Calibrating vessels, 144, 116.
 Caliche, 210, 163.
 Calomel, 425, 419.
 Carbohydrates, 350, 305.
 Carbon, 308, 275.
 — amorphous, 310, 275.
 — combining weight of, 313, 276.
 — dioxide, 315, 279.
 — disulphide, 251, 207.
 — monoxide, 320, 282.
 Carbonates, 318, 281.
 Carbonic oxide, 320, 282.
 Carbonyl chloride, 323, 283.
 — sulphide, 252, 208.
 Carborundum, 358, 315.
 Catalysis, 154, 117 ; 156, 117.
 Caustic soda, 398, 353.
 Cavendish's experiments, 61, 54.
 Cellulose, 350, 305.
 Cement, hydraulic, 411, 380.
 Chalk, 413, 384.
 Changes, chemical and physical, 14, 12 ; 53, 47.
 Charcoal, 310, 275.
 — animal, 311, 275.
 — combustion of, 2, 4.
 Chemical changes, 14, 12 ; 53, 47.
 — action, 49, 43-46.
 — compound, 45, 40.
 Chlorates, 202, 151.
 Chloride of lime, 199, 150.
 Chlorine, 184, 135.
 — bleaching by, 187, 136.
 — bromide of, 209, 160.
 — monoxide, 199, 149.
 — peroxide, 203, 154.
 Chromates, 450, 484.
 Chrome alum, 449, 482.
 Chromic anhydride, 449, 483.
 — chloride, 448, 478.
 — oxide, 448, 480.
 — sulphate, 449, 481.
 Chromium, 447, 476.
 — trioxide, 449, 483.
 Chromous chloride, 448, 477.
 — oxide, 448, 479.
 Chromyl chloride, 450, 484.
 Classification of matter, 45, 40.
 Clay, 355, 310.
 Cleavage, 384, 337.
 Coal gas, 347, 303.
 Cobalt, 472, 520.
 — and nickel, 471, 519.
 Cobaltic oxide, 472, 524.
 Cobaltous chloride, 472, 522.
 — oxide, 472, 521.
 — sulphate, 472, 523.
 Coke, 311, 275.
 Combination, 49, 43 ; 112, 100.
 Combining weights, 97, 84.
 Combustion, 2, 3 ; 84, 71.
 — inverted, 85, 72.
 — supporters of, 85, 72.
 Compounds, chemical, 45, 40.
 Conservation of mass, 6, 6.
 Constants, physical, 24, 25.
 Copper, 389, 340 ; 474, 529.
 — extraction from ores, 475, 530.
 — hydride, 302, 264 ; 476, 533.
 Copper nitrate, 138, 115 ; 478, 540.
 — ores of, 474, 529.
 — sulphate, 137, 115.
 Copperas, 461, 499.
 Coprolite, 286, 248.
 Corrosive sublimate, 426, 420.
 Critical temperature, 173, 130.
 Cryolite, 223, 175.
 Crystallization, purification by, 40, 37.
 — water of, 55, 50.
 Crystals, 383, 337.
 — classification of, 384, 339.
 — preparation of, 38, 36 ; 94 *d*.
 Cupric arsenite, 479, 544.
 — carbonates, 478, 541.
 — chloride, 478, 543.
 — nitrate, 478, 540.
 — oxide, 477, 536.
 — sulphate, 478, 539.
 Cuprous chloride, 477, 537.
 — iodide, 477, 538.
 — oxide, 476, 535.
 — sulphide, 478, 542.
 Cyanates, 330, 289.
 Cyanides, estimation of, 326, 285.
 Cyanogen, 329, 287.
 — chloride, 329, 288.
 Cyanuric chloride, 329, 288.

- Deacon's process, 190, 138.
 Decay, 94, 79.
 Decomposition, 49, 44.
 — double, 52, 46 ; 113, 100.
 Density, 25, 28.
 — influence of temperature on, 28, 29.
 Dialysis, 354, 309.
 Diamond, 309, 275.
 Diffusion of gases, 170, 129.
 — of liquids, 37, 35.
 Dimorphism, 384, 338.
 Dissociation, 244, 198 ; 265, 220.
 — electrolytic, 373, 331.
 Distillation, destructive, 25, 27.
 — fractional, 24, 26.
 — of water, 8, 8.
 Dolomite, 418, 405.
 Dumas's experiments, 65, 56.
 Dutch liquid, 345, 301.

 Electrolysis, 49, 44 ; 370, 328.
 Electrolytic dissociation, 373, 331.
 Electroplating, 290, 341.
 Elements, 45, 40 ; 127, 109 ; 494, 562.
 Emanation of radium, 493, 563.
 Endothermic compounds, 368, 326.
 Energy, conservation of, 96, 81.
 — of radium, 494, 562.
 Epsom salts, 418, 404.
 Equations, 112, 100.
 Equivalent of calcium hydroxide, 153 *c*, 116.
 — of carbonate of soda, 151, 116.
 — of soda, 150, 116.
 — weights, 97, 84.
 Equivalents, electro-chemical, 372, 330.
 — of acids, 149, 116.
 Ethane, 335, 293.
 Ether, 342 *b*, 300.
 Ethylenc, 344, 301.
 — dichloride, 345, 301.
 Evaporation, 6, 7.
 Exothermic compounds, 368, 326.
 Experiment, errors of, 17, 17.
 Explosives, 272, 230.

 Fats, 337, 295.
 Felspar, 355, 310.
 Fermentation, 342 *a*, 297 ; 342 *d*, 299.
 Ferments, 342 *b*, 297.
 Ferrates, 461, 498.
 Ferric chloride, 139, 115 ; 463, 501.
 Ferric oxide, 460, 496.
 — sulphate, 462, 499.
 Ferrieyanides, 331, 290.
 Ferrocyanides, 331, 290.
 Ferrous carbonate, 464, 504.
 — chloride, 463, 500.
 — iodide, 139, 115 ; 464, 502.
 — sulphate, 461, 499.
 — sulphide, 464, 503.
 Fire, chemistry of, 1, 2.
 Flame, structure of, 86, 73.
 Flames, luminosity of, 88, 74.
 Fluorides, 221, 173.
 — metallic, 222, 174.
 Fluorine, 220, 172.
 Fluorspar, 219, 171 ; 412, 382.
 Foods, 351, 306.
 Formule, graphic, 125, 107.
 — and symbols, 111, 99 ; 117, 103.
 Fraunhofer's lines, 382, 336.

 Galena, 440, 452.
 Gallium, 431, 433.
 Gases, kinetic theory of, 173, 131.
 — liquefaction of, 172, 130.
 — occlusion of, 488, 558.
 — preparation of, 94 *c*.
 Germanium, 441, 458.
 Glass, 356, 311.
 Glauber's salt, 399, 356.
 Glucinum, 417, 399.
 Glycerin, 337, 295.
 Glycerol, 337, 295.
 Gold, 485, 555.
 — chlorides, 487, 557.
 — oxides, 486, 556.
 Graphite, 309, 275.
 Green vitriol, 461, 499.
 Gun-cotton, 272, 229 ; 273, 230.
 Gunpowder, 272, 230.

 Hardness of water, 11, 11 ; 342.
 — temporary and permanent, 12, 11.
 Heats of combustion, 366, 323.
 — of formation, 367, 324.
 — of neutralization, 367, 325.
 Heat, action of, 94 *g*.
 Helium, 381, 336.
 Homologous series, 335, 294.
 Hydrazine, 267, 221.
 Hydrocarbons, 332, 291.
 Hydrogen bromide, 206, 157.
 — fluoride, 221, 173.
 — iodide, 214, 166.

- Hydrogen nitride, 267, 223.
 — peroxide, 68, 58.
 — persulphide, 232, 184.
 — preparation of, 167, 125.
 — properties of, 168, 126.
 — recognition of, 49, 45.
 — sulphide, 229, 183.
 Hydrolysis, 342 *c*, 298.
 Hydroxides, metallic, 395, 346.
 Hydroxylamine, 267, 222.
 Hyponitrites, 280, 241.
 Hypothesis of Avogadro, 103, 91.

 Ice, latent heat of fusion of, 15, 14.
 — melting-point of, 15, 13.
 Ignition, 84, 70.
 Indicators, 146, 116.
 Incandescence, 84, 70.
 Indestructibility of matter, 5, 5.
 Indium, 431, 434.
 Iodates, 217, 169.
 Iodic anhydride, 217, 169.
 Iodides, metallic, 215, 167.
 Iodine, 210, 163.
 — monochloride, 219, 170.
 — trichloride, 219, 170.
 Iron, 391, 341; 452, 486.
 — extraction from ores, 453, 488.
 — ores, 452, 487.
 — oxides, 460, 495.
 — valency of, 464, 505.
 Isomorphism, 384, 338.

 Kinetic theory of gases, 173, 131.

 Lampblack, 310, 275.
 Latent heat of vaporization, 16, 16.
 Laughing gas, 279, 240.
 Lavoisier, researches in combustion, 2, 4.
 Law of Boyle, 74, 63.
 — of Charles, 75, 64.
 — of constants, 68, 57; 95, 80.
 — of Dalton, 376, 333.
 — of Dulong and Petit, 109, 95; 110, 96.
 — of even numbers, 277, 238.
 — of volumes of Gay-Lussac, 97, 83.
 — of Graham, 171, 129; 175, 131.
 — of Henry, 376, 333.
 — of multiples, 70, 59; 95, 80.
 — periodic, 179, 133; 180, 134.
 — — table of, 181.
 — of reciprocals, 97, 82.

 Laws of electrolysis, 372, 330.
 Lead, 389, 340; 392, 341; 436, 444.
 — acetate, 440, 455.
 — alloys of, 438, 445.
 — and silica, 440, 456.
 — carbonate, 440, 457.
 — dichloride, 438, 446.
 — dioxide, 439, 451.
 — gain of weight when burnt, 2, 3.
 — nitrate, 138, 115; 440, 453.
 — perchloride, 438, 447.
 — sulphate, 440, 454.
 — sulphide, 440, 452.
 Leather, 342 *h*, 299.
 Leblanc process, 400, 357.
 Life, animal, processes of, 90, 76.
 Lime, 410, 380.
 Lime, slaked, 412, 381.
 Limestone, 413, 384.
 — rock, corrosion of, 13, 11.
 Lithium, 397, 348.
 Lunar caustic, 483, 549.

 Magnesia, 417, 402.
 Magnesium, 417, 400.
 — carbonate, 418, 405.
 — chloride, 417, 401.
 — gain of weight when burnt, 2, 3.
 — oxide, 417, 402.
 — phosphate, 419, 406.
 — sulphate, 418, 404.
 — sulphide, 418, 403.
 Manganese, 465, 506.
 — alum, 465, 509.
 — dioxide, 466, 510.
 Manganic chloride, 467, 514.
 — oxide, 466, 509.
 — sulphate, 467, 512.
 Manganous chloride, 467, 513.
 — oxide, 465, 507.
 — sulphate, 466, 511.
 — sulphide, 467, 515.
 Marsh gas, 332, 291.
 Matter, classification of, 45, 40.
 — conservation of, 95, 80.
 — constitution of, 101, 88.
 — indestructibility of, 5, 5.
 Melting-points, determination of, 18, 19.
 — table of, 19, 19.
 Mercuric chloride, 426, 420.
 — iodide, 139, 115.
 — nitrate, 426, 423.

- Mercuric oxide, 425, 418.
 — sulphate, 426, 425.
 — sulphide, 427, 426.
 Mercurous chloride, 425, 419
 — iodide, 139, 115.
 — nitrate, 426, 423.
 — oxide, 424, 417.
 — sulphate, 426, 424.
 Mercury, 388, 340; 423, 414.
 Metalloids, 131, 109.
 Metals, characters of, 127, 109.
 — action of water on, 58, 52.
 — and acids, 129, 109.
 — electrical relation of, 130, 109.
 Methane, 332, 291.
 Milk, 342, 295.
 Mixtures, 46, 42.
 Molecular weights, 104, 91; 105, 92.
 Molecules, 103, 90.
 Mortar, 411, 380.

 Nascent state, 188, 137.
 Natural waters, solids in, 9, 9; 10, 9.
 Nessler's test, 264, 219.
 Nickel, 473, 525.
 — and cobalt, 471, 519.
 — oxide, 473, 526; 474, 528.
 — sulphate, 473, 527.
 Nitration, 272, 229.
 Nitre, 269, 225.
 Nitric anhydride, 275, 234.
 — oxide, 278, 239.
 — peroxide, 276, 237.
 Nitrification, 405, 362.
 Nitrites, 275, 236.
 Nitrogen, 71, 61; 256, 213.
 — and plants, 258, 215.
 — chloride, 268, 224.
 — detection in compounds, 281, 344.
 — iodide, 269, 224.
 — monoxide, 279, 240.
 — pentoxide, 275, 234.
 — tetroxide, 276, 237.
 — trioxide, 275, 235.
 Nitro-glycerin, 272, 229; 273, 230.
 Nitrosyl chloride, 281, 243.
 Nitrous anhydride, 275, 235.
 — oxide, 279, 240.
 Nomenclature, 115, 102.
 Non-metals, characters of, 127, 109.
 Nordhausen sulphuric acid, 238, 193.
 Oils and fats, 337, 295.
 Oils, mineral, 337, 295.
 Oil of vitriol, 238, 194.
 Olefiant gas, 344, 301.
 Osmotic pressure, 376, 335.
 Oxidation, 61, 53; 176, 132.
 Oxides, basic, 134, 112.
 — classes of, 158, 120.
 — metallic, preparation of, 153 *i*; 393, 343; 394, 344, 345.
 — of metals, 128, 109.
 — of non-metals, 128, 109.
 Oxygen, an element, 161, 122.
 — atomic weight of, 161, 123.
 — detection of, 160, 121.
 — preparation of, 154, 117.
 — properties of, 157, 118.
 Oxygen, recognition of, 160, 121.
 Oxyhydrogen flame, 170, 128.
 Ozone, 162, 124.

 Paracyanogen, 329, 287.
 Paraffins, 335, 293; 337, 295.
 Parkes' process, 481, 545.
 Pattinson's process, 481, 545.
 Periodates, 218, 169.
 Phosgene gas, 323, 283.
 Phosphine, 289, 251.
 Phosphonium, 291, 252.
 Phosphoric anhydride, 293, 257.
 — oxide, 293, 257.
 Phosphorous anhydride, 299, 262.
 — chloride, 291, 253.
 — oxide, 299, 262.
 Phosphorus, 282, 245.
 — atomic weight of, 288, 250.
 — iodide, 293, 256.
 — oxychloride, 292, 255.
 — pentachloride, 292, 254.
 — pentafluoride, 293, 256.
 — red, 285, 246.
 — sulphides, 302, 266.
 — tetroxide, 302, 265.
 — trichloride, 291, 253.
 — trifluoride, 293, 256.
 Phosphoryl trichloride, 292, 255.
 Phosphuretted hydrogen, 289, 251.
 Photography, 484, 554.
 Physical changes, 14, 12; 53, 47.
 — constants, 24, 25.
 Pig-iron, 455, 490.
 Pipette, calibration of, 54, 48.
 Plants and atmosphere, 91, 77.
 — and nitrogen, 258, 215.
 Plaster of Paris, 413, 385.

- Platinic chloride, 488, 560.
 Platinum, 389, 340; 487, 558.
 — oxides, 488, 559.
 Plumbic oxide, 439, 449.
 Plumbous oxide, 439, 448.
 Polonium, 490, 561.
 Porcelain, 356, 310.
 Potassium, 403, 359.
 — bicarbonate, 406, 364.
 — bromide, 407, 368.
 — carbonate, 405, 363.
 — chlorate, 202, 151.
 — cyanate, 326, 285.
 — cyanide, 325, 285.
 — ferrocyanide, 325, 285.
 — hydrogen tartrate, 406, 365.
 — hydroxide, 404, 360.
 — iodide, 407, 367.
 — manganate, 467, 516.
 — nitrate, 405, 362.
 — oxides, 404, 359.
 — permanganate, 467, 516.
 — sulphate, 404, 361.
 — sulphides, 406, 366.
 — thiocyanate, 325, 285.
 Pottery, 355, 310.
 Precipitation, 139, 115.
 Precipitates, collecting, 153 *b*.
 Pressure, influence on boiling-point,
 20, 21.
 Proteids, 351, 306.
 Prout's hypothesis, 179, 133.
 Prussian blue, 325, 285.

 Quicklime, 410, 380.

 Radicles, compound, 123, 105.
 — — valency of, 124, 106.
 Radiation of radium, 492, 562.
 Radio-activity, 490, 561.
 Radium, 490, 561.
 Red lead, 439, 450.
 Reduction, 61, 53; 176, 132.
 Replacment, 49, 45.
 Respiration, 90, 76.
 Rubidium, 407, 370.

 Sal-ammoniac, 260, 217; 408, 372.
 Salt, making, 136, 115.
 Salts from acids and alkalis, 94 *c*.
 — spirit of, 191, 141.
 Salt-cake process, 400, 357.
 Salts, 135, 113.
 — acid, 135, 114.

 Salts, nature of, 135, 113.
 Saponification, 338, 295.
 Scheele's green, 304, 269; 479, 544.
 Selenion, 252, 210.
 Silica, 353, 307.
 Silicates, 355, 310.
 Silicon, 357, 312.
 — carbide, 358, 315.
 — chloride, 358, 316.
 — fluoride, 222, 175.
 — hydrides, 357, 313.
 — nitrides, 357, 314.
 Silver, 389, 340.
 — allotropic, 482, 546.
 — extraction from lead, 480, 545.
 Silver, determining, 153 *k* and *l*.
 Slaked lime, 412, 381.
 Soap, 338, 295.
 Soda crystals, 400, 357.
 — ash, 400, 357.
 Sodamide, 267, 223.
 Sodium, 397, 349.
 — bicarbonate, 403, 358.
 — carbonate, 400, 357.
 — chloride, 398, 351.
 — dioxide, 399, 354.
 — hydride, 399, 355.
 — hydroxide, 398, 353.
 — monoxide, 398, 352.
 — sulphates, 399, 356.
 — sulphides, 399, 356.
 Solids, in natural waters, 9, 10.
 Solids, solubility, 94 *a*.
 Solidification, evolution of heat on,
 15, 14.
 Solubilities, table of, 141.
 Solubility curves, 35, 34; Appendix.
 — influence of temperature on, 34,
 33.
 — of liquids in liquids, 376, 334.
 — of solids in liquids, 94 *a*; 376, 334.
 Solution, nature of, 58, 51.
 Solutions, 375, 332.
 — standard, 149.
 Specific gravity, determination of, 31,
 31.
 — heat and atomic weight, 108, 95.
 — heats, table of, 109, 95.
 Spectroscope, 379, 336.
 Spectrum analysis, 379, 336.
 Spirit, absolute, 342 *a*.
 — methylated, 342 *d*, 298.
 — of hartshorn, 260, 217.
 — proof, 342 *c*, 298.

- Spirit, rectified, 342 *c*, 298.
 Standard solutions, 149; 153 *g*.
 Stannic oxide, 435, 441.
 Stannous oxide, 435, 440.
 Starch, 342 *c*, 298.
 State, nascent, 188; 137.
 Steel, 460, 493.
 Stibine, 443, 460.
 Strontia, 414, 390.
 Strontium, 414, 389.
 — carbonate, 415, 394.
 — chloride, 415, 391.
 — dioxide, 415, 390.
 — monoxide, 414, 390.
 — nitrate, 415, 393.
 — sulphate, 415, 392.
 Substitution, 49, 45; 113, 100.
 Sugars, 351, 305.
 Sulphates, 246, 201.
 Sulphides, 233, 185.
 Sulphites, 236, 190.
 Sulphur, 225, 178.
 — allotropic forms of, 227, 181.
 — dioxide, 233, 187.
 — halides, 252, 209.
 — heptoxide, 248, 204.
 — oxides and acids of, 233, 186.
 — sesquioxide, 248, 202.
 — trioxide, 237, 191.
 Sulphuretted hydrogen, 229, 183.
 Sulphuric anhydride, 237, 191.
 Symbols and formulæ, 111, 99; 117, 103.
 Synthesis, 49, 43.

 Tannin, 342 *h*, 299.
 Tanning, 342 *h*, 299.
 Tartar emetic, 445, 467.
 Tellurium, 254, 211.
 Thallium, 431, 435.
 Thorium, 490, 561.
 Tin, 433, 437.
 — alloys of, 434, 438.
 — chlorides, 434, 439.
 — monoxide, 435, 440.
 Tungsten, 447, 475.

 Uranium, 447, 475; 490.

 Valency, 121, 104.
 Vaporization, latent heat of, 16, 13.
 Vermilion, 427, 426.
 Vinegar, 342 *d*, 299.
 Volume, atomic, 183, 134.
 — specific, 182, 134.
 Volumetric analysis, 144.

 Washing soda, 400, 357.
 Water, 6, 7.
 — boiling-point of, 16, 15.
 — chemical properties of, 55, 49.
 — composition of, 42, 39.
 — — by volume, 61, 54.
 — — by weight, 64, 55.
 — dissolved solids in, 9, 9.
 — dissolved air in, 7, 7.
 — distillation of, 8, 8.
 — electrolysis of, 43, 39.
 — gas, 322, 282.
 — hardness of, 11, 11; 342, 285.
 — physical properties of, 54, 48.
 — river, 10, 10.
 — sea, composition of, 10, 9.
 — softening, 13, 11.
 — spring, 10, 10.
 — vapour, pressure of, 22, 23.
 — of crystallization, 55, 50; 94 *f*.
 Waters, natural, 9, 9.
 Weldon's process, 191, 139.
 White lead, 440, 457.
 — vitriol, 421, 411.
 Wine, 342 *b*, 298.
 Wood, 350, 305.
 Wrought iron, 456, 491.

 Yeast, 342 *b*, 297.

 Zero, absolute, 76, 65.
 Zinc, 419, 407.
 — alloys of, 421, 408.
 — carbonate, 421, 412.
 — chloride, 421, 409.
 — oxide, 421, 410.
 — sulphate, 137, 115; 421, 411.
 — sulphide, 421, 413.

ANSWERS

Mr. H. C. Lacell has kindly prepared the following Answers to the problems. The atomic weights used have since been revised in certain cases, but the errors thus introduced should not be a source of difficulty to the student.

Answers to problems on p. 63.

1. 165 c.c. of O_2 . 2. 120 c.c. of N_2 . 40 c.c. of H_2 . 3. 21 per cent.
 4. 2,785 c.c. of air. 2,228 c.c. of N_2 . 5. $\left\{ \begin{array}{l} \text{Oxygen} \quad 20.96 \\ \text{Nitrogen} \quad 79.04 \\ \hline 100.00 \end{array} \right.$

Answers to problems on p. 78.

1. 285.7 c.c. 2. 1,042 c.c. 3. 75.37 c.c. 4. 150 c.c.
 5. 71.04 litres. 6. $3,913^\circ$. 7. 548.3 c.c. 8. 1,111 c.c.
 9. 80° .

Answers to problems on p. 100.

1. 11.99. 2. 32.53. 3. 31.81. 4. 32.68. 5. 3. 6.

Answers to problems on pp. 499-504.

1. 214.4. 230.1. 121.7. 97.4.
 2. 320.6. 846.6. 35.8. 496. 31.3. 116.2. 137.6. 158.9. 79.
 3. 6.997 grams. 4. $\left\{ \begin{array}{l} \text{Hydrogen} \quad 11.18 \\ \text{Oxygen} \quad \quad 88.82 \\ \hline 100.00 \end{array} \right.$ 5. 339.7. 6. 421 grams.
 7. 45.7. 8. 13.13 grams. 9. $\left\{ \begin{array}{l} \text{Carbon} \quad 52.08 \\ \text{Hydrogen} \quad 13.13 \\ \text{Oxygen} \quad \quad 34.79 \\ \hline 100.00 \end{array} \right.$ 10. 99.28 grams.
 11. $\left\{ \begin{array}{l} \text{Potassium} \quad 31.87 \\ \text{Chlorine} \quad 28.93 \\ \text{Oxygen} \quad \quad 39.20 \\ \hline 100.00 \end{array} \right.$ 12. 16 times. 13. 5.66 grams.
 14. 25.16 per cent. 15. 44.9 grams. 16. 53.19 grams.
 17. 1753.2 grams of H_2SO_4 . 1168.2 grams of Zn. 18. 115.2 grams.
 19. 17.6 grams. 20. 528.3 litres. 21. FeO .
 22. CH_2O (Probl. 3, p. 115, $C_2H_4O_2$). 23. $C_2H_3O_3$. 24. 89.23 litres.

25. 12.51 litres of H_2 . 6.25 litres of O_2 . 26. 3.52 litres.
27. 787 c.c. 28. $\left\{ \begin{array}{l} \text{Hydrogen } 11.08 \\ \text{Oxygen } 88.92 \\ \hline 100.00 \end{array} \right.$ 29. $FeSO_4, 7H_2O$.
30. $C_{12}H_{22}O_{11}$. 31. $C_2H_4O_2$. 32. 7.98. 33. 12.5.
34. 32. 35. 55.72. 36. 196.1.
37. Equivalent 8.98. At. wt. 26.96. Valency 3. 39. 31.6. 40. 32.
41. .047. 42. 2.8 c.c. 43. 100.3 c.c. 44. 10.02 litres.
45. 106.1 grams of O_2 . 270.7 grams of $KClO_3$. 46. 2.026 grams.
47. 5.12 litres. 48. 205.9 grams. 49. 25.56 c.c. 50. 125.0 grams.
51. PbO . 53. 59.5. 119. 54. 26.77. 55. 62.48.
56. 43.77. 57. 28.07. 58. 1.59 grams.
59. 14.5 c.c. of N_2 . 8.25 c.c. of O_2 . 60. 969.2 grams.
61. 4.95 grams. 62. 62.5 grams. 63. 71 per cent.
64. 0.25 grams. 65. 14.3 grams of KHO . 95.4 grams of H_2O .
66. 319.6 grams. 67. 5.78 per cent. 68. 56 grams. 119.6 litres.
69. 88.88 c.c. 70. (a) 150 c.c. (b) 600 c.c. 71. 2,500 grams.
72. 35.04 per cent.
73. 2,947 c.c. of CO_2 . 5,894 c.c. of SO_2 . 12.16 litres of O_2 . 79 litres of N_2 .
74. 270 grams. 267.8 grams. 75. $\left\{ \begin{array}{l} \text{Marsh gas } 38.46 \\ \text{Carbon monoxide } 61.54 \\ \hline 100.00 \end{array} \right.$
76. 3.5 c.c. of CH_4 . 2.8 c.c. of C_2H_4 .



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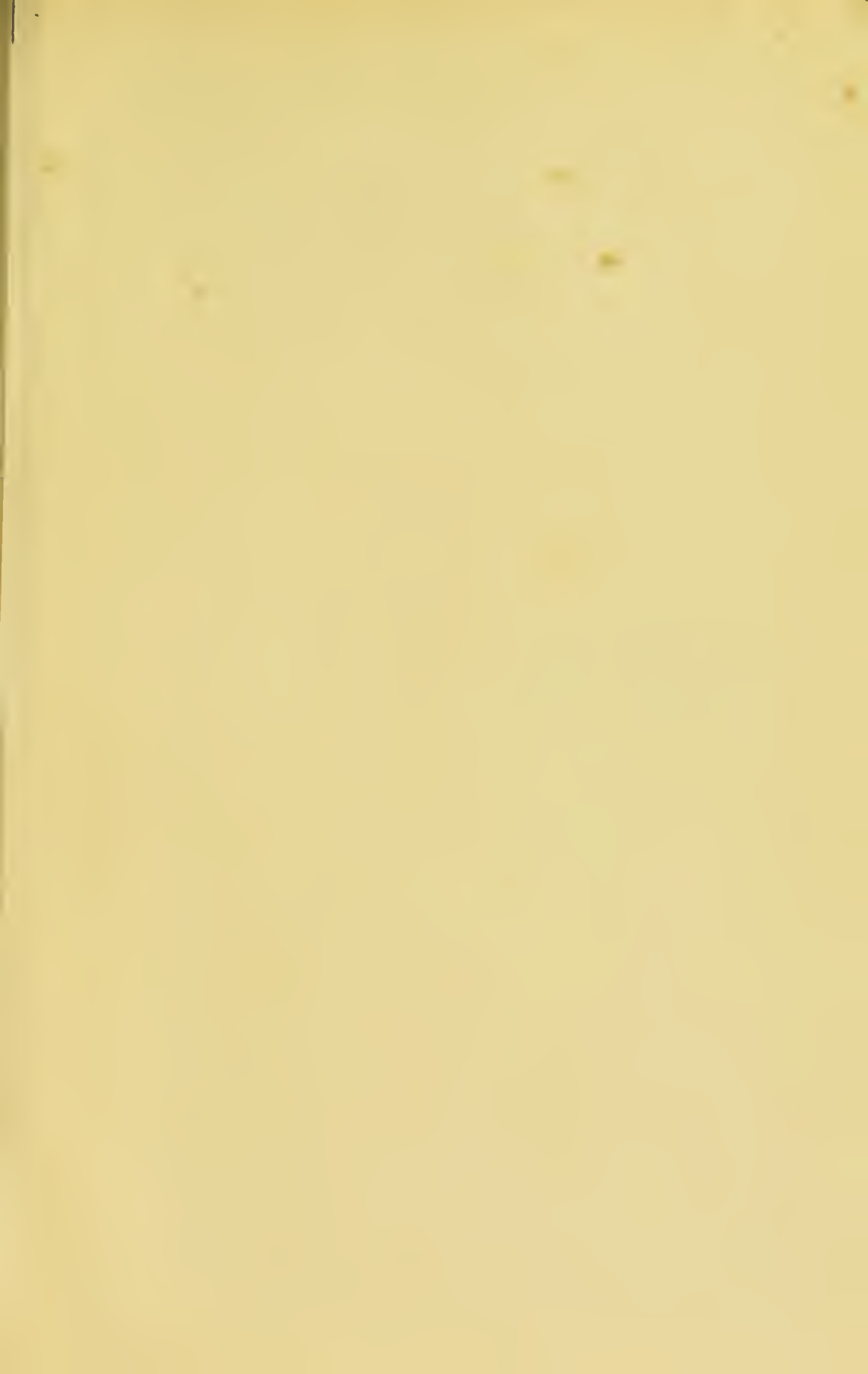
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